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ANALYSIS OF STACK GAS POLLUTANTS BY GAS CHROMATOGRAPHY

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FINAL REPORT

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ANALYSIS OF STACK GAS POLLUTANTS BY GAS CHROMATOGRAPHY

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ABSTRACT

A critical literature survey of the available information on stack gas pollutants was conducted. Pertinent references related directly to the gas chromatographic resolution of stack gas components have been abstracted in this report. A number of gaseous components found in stack gases have been resolved chromatographically, but as yet no single column or series of columns is capable of resolving more than several closely related compounds.

The construction of a sensitive gas chromatographic analysis unit with a $\pm$ 0.1°C constant temperature column compartment and a constant voltage power supply with a 3 μv noise level is described, including sketches and electric circuit diagrams. A gas mixing apparatus, making use of Dalton's Law of partial pressures, is available to prepare multi-component mixtures in the p.p.m. range, with an accuracy of one per cent.

Experimental results obtained from packed and capillary columns are discussed separately. Hydrogen sulfide, sulfur dioxide and methyl mercaptan were resolved by Silicone Oil 550, Triton X-100, and dibutyl phthalate coated packed columns. Nitrous oxide, nitrogen dioxide, ammonia, methane and carbon monoxide were also resolved on various partition columns. Methods for quantitative calibration and the evaluation of an analysis are discussed. Quantitative results obtained with H_2S, SO_2 and CH_3SH are presented along with recommendations for further work in this field.

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GLOSSARY OF TERMS

A = Total area of peaks

C_1 = Chart speed

C_2 = Recorder sensitivity

C.F.R. = Corrected flow rate = (F.R.) (f_t) (f_m) (f_p)

C.S. = Complete separation

d_i = Distance on graph from injection point to peak maximum

f_m = Moisture correction factor =

$$\frac{\text{Atm. press. - vapor pressure of } H_2O \text{ at flow meter temp.}}{\text{atmospheric pressure}}$$

f_p = Pressure correction factor =

$$\frac{3}{2} \times \frac{(P_{ia}/14.3)^2 - 1}{(P_{ia}/14.3)^3 - 1}$$

f_t = Temperature correction factor =

$$\frac{\text{Column temp. + 273.2}}{\text{Flow meter temp. + 273.2}}$$

F.R. = Flow rate (uncorrected)

I.S. = Incomplete separation

N = Number of theoretical plates =

$(4 \frac{d}{w})^2$, using consistent units

N.S. = No separation

P_{ia} = Inlet pressure, p.s.i.a.

R = Separation factor = $\frac{2(d_2 - d_1)}{w_1 + w_2}$, using consistent units

R.T. = Retention time

R.V. = Retention volume = (R.T.) (C.F.R.)

S = Sensitivity = $\frac{(A)(F.R.)}{(V)(C_1)(C_2)}$, using consistent units

V = Sample volume

V_g^o = Specific retention volume = R.V./total gms coating liquid

w_i = Base width of peak

I. STATEMENT AND PURPOSE OF THE RESEARCH

To evaluate hazards of the environment due to noxious gases, investigate contamination from a process or a source and appraise the performance of control equipment, it is essential to determine the quality and quantity of stack gas components discharging from industrial processes. The lack of a simple and interference free method for gas analysis has prevented the establishment of precise relationships to support experimental evidence and theory. More refined and simpler measurement techniques for gaseous air pollutants are needed. This need includes methods for evaluating instantaneous peak stack emissions and the development of continuous monitoring equipment to indicate any increase in the concentration of gaseous contaminants.

The oxides of sulfur and nitrogen comprise some of the most harmful and insidious pollutants of the atmosphere resulting from stack gases. Immediate physiological damage, due to individual gas components, is difficult to trace or to prove. The toxicity of sulfur dioxide has been studied intensively and two recent articles (1)(2) implicate low SO_2 concentrations as affecting the blood protein serum of rabbits and in children. Industrial stack gases are one of the major sources of air pollution and have often become of public concern and a target of local air pollution legislation.

The sulfur-bearing contaminants hold a special position in nearly all air pollution investigations. The analysis and collection of sulfur-bearing components, such as SO_2, H_2S and mercaptans are of particular interest. Automatic recording instruments have become available but these employ "wet methods" of analysis, subject to their inherent errors due to interference between components and giving only average concentrations over

a prolonged sampling period. Research conducted in recent years has shown that under certain conditions oxides of nitrogen can participate in the photochemical reactions that lead to the production of ozone and the formation of "smog".

Gas chromatography, a new but rapidly developing analytical method for qualitative and quantitative gas analysis, shows promise as a precise tool free from interfering error for the separation, detection, and identification of gases such as sulfur dioxide, mercaptans, hydrogen sulfide and oxides of nitrogen, from a single stack gas sample.

It was the purpose of these investigations to develop a gas chromatographic method for the detection of small concentrations of air pollutants in stack gases and for the measurement of their instantaneous peak concentrations. To make the analysis qualitative as well as quantitative, specific retention volumes needed careful evaluation to permit accurate identification of the individual components from an unknown sample.

The results described in this report cover a two and one half year period from December 1, 1959 to May 15, 1962. The first year of this program was primarily devoted to (a) a critical literature survey, (b) the construction of a more sensitive chromatographic unit, (c) the design and development of a static gas mixing device, and (d) a study of packed and capillary columns for which resolution data will be presented. The latter part of the program was devoted toward completion of the qualitative studies, toward optimizing columns and quantitative calibration of the columns for the component gases.

II. LITERATURE SURVEY

In the rapidly advancing field of air pollution abatement control, relatively little effort has been expended toward the application of gas chromatography for the analysis of stack gas pollutants. Although considerable information has become available about the gases giving rise to air pollution problems and an increasing array of instruments has become available for the determination of many components found in stack gases, there has not, as yet, been found one instrument which is able to identify more than a few components. The gas chromatographic method of analysis lends promise to provide an answer to this problem. A number of gaseous components found in stack gases have been quantitatively and qualitatively identified, but as yet no single column or series of columns is capable of resolving more than a few closely related compounds.

A carefully conducted survey of existing literature has revealed that carbon monoxide was detected in a concentration as low as 50 p.p.m. in methane and air by Coppens and Bricteaux (3) using a 50 cm long molecular sieve, type 5A, at 25°C. The same investigators (4) also analyzed CO_2 in concentrations as low as 30 p.p.m. in the presence of CO_2 by removing the CO_2 with NaOH on an asbestos mat and then converting the CO to CO_2 by passing it through I_2O_5 at 115°C and analyzing on a silica gel column. Greene, et al., (5) analyzed CO in a complex mixture using dual columns of 9 ft charcoal and 20 ft alumina with temperature programming. Smith, et al., (6) analyzed CO and CO_2 using two layers of silica gel, separated by a layer of iodine pentoxide, operated at 115°C.

Some work has been done to separate, detect and identify oxides of sulfur and other sulfur compounds. Outstanding among this group has

been the work conducted by Adams, et al, (7)(8)(9), at the University of Washington. Their research was particularly successful in resolving hydrogen sulfide, sulfur dioxide and mercaptans from pulp and paper mill effluents. Triton X-305 was found to be the best coating material for these gaseous effluents. Sullivan (10) analyzed mercaptans and sulfides using a non-linear temperature programmed squalane column. Spencer, et al, (11) also separated sulfides and mercaptans operating a di-n-phthalate column at 50°C. H_2S and mercaptans were analyzed by Kyce and Bryce (12) using a tri-cresyl phosphate column and temperature technique. Retention times for H_2S and C_1 to C_4 mercaptans on Carbowax 1540 and Apiezone M columns were reported by Carson, et al, (13). Ottenstein (14) analyzed H_2S and SO_2 in permanent gases using dual columns of HMPA and molecular sieves type 13X.

It has been shown that under certain conditions, oxides of nitrogen can participate in the photochemical reactions that lead to the formation of smog. Consequently, in recent years emphasis has been placed on the identification of the oxides of nitrogen. It is hoped that current research will make possible sound measurements to survey and to prevent pollution of the air. The resolution of nitrous oxides has been reported by Smith, et al, (6). Nitric and nitrous oxides were analyzed by Szulczewski and Higuchi, (15), using a cooled down and then re-heated six foot silica gel column. Lefort and Tarrago (16) separated N_2 and NO on alumina and calcium silicate columns. Greene and Pust (17) analyzed NO_2 by converting it to NO on a wetted Linde molecular sieve column. Smith, et al, (18) found that the Greene and Pust method (17) was unsuccessful in the presence of O_2 and therefore swept the N_2 and O_2 out of the sample during immersion in an acetone-dry ice bath. They then vaporized and analyzed the frozen NO_2.

Janak and Rusek (19) separated N_2O successfully on activated carbon and silica gel columns. Sakaida, et al., (20), analyzed NO in the range of 1,000 - 10,000 p.p.m. on a specially designed 8 ft silica gel column.

As far as could be determined no gas chromatographic analysis work has been done on nitrogen trioxide or nitrogen pentoxide. Similarly, it was not possible to find any published reports on the identification of ozone or sulfur trioxide by gas chromatography.

In a rapidly moving field, such as the application of gas chromatography to solve air pollution problems, it is important that no aspect whether close or far removed, be left uncovered. Therefore, the survey of the current literature included a number of related aspects which sooner or later might have become associated with our own research efforts. In fact, two of these were under serious consideration to assist in the further development of the gas chromatographic technique for stack gas analysis when the project was terminated. The various related aspects, covered in this survey, included the following: (a) flame spectrophotometry, (b) ionization detection (21) in lieu of thermal conductivity detection, (c) temperature programming, (d) freeze-out techniques to remove water vapor; and (e) capillary columns with high theoretical plate numbers to increase the sensitivity of detection.

III. EXPERIMENTAL APPARATUS

A. The Chromatographic Unit

The basic gas chromatographic unit is composed of a column, detection system, and an automatic 0 - 1 millivolt recorder.

Reproducibility of the peak heights or areas, important for the qualitative analysis of the various components present in stack gas, requires that the column compartment be carefully temperature regulated. The column, which consists of polyethylene tubing packed with liquid-coated firebrick, is coiled around a specially designed frame to insure adequate circulation of air to maintain a uniform temperature throughout the 15 in x 15-1/2 in column compartment, as is shown in Figure 1. The 150 watt heater, actuated by a Fenwall thermostat, controls the compartment temperature within a range of less than $\pm$ 0.1°C over a period of several hours, compatible with an ambient room temperature variation of $\pm$ 1°C.

A thermistor-type thermal conductivity cell was chosen as the detector because of its sensitive response to all component gases involved in this study. Ionization of flame detectors, while they are very sensitive to hydrocarbon vapors, do not respond to air, carbon monoxide, carbon dioxide, hydrogen sulfide, sulfur dioxide, and nitrogen oxides. In the relatively low temperature range under which these studies are conducted (room temperature to 100°C), a thermistor-type thermal conductivity cell is generally three to four times more sensitive than a filament (hot wire) type of detector (22)(23)(24). The thermistor cell, because of its greater temperature dependence, requires improved temperature control to maintain a stable base line. As may be seen in Figure 2, a separate detector compartment with heater, fan and thermostat is provided to maintain the

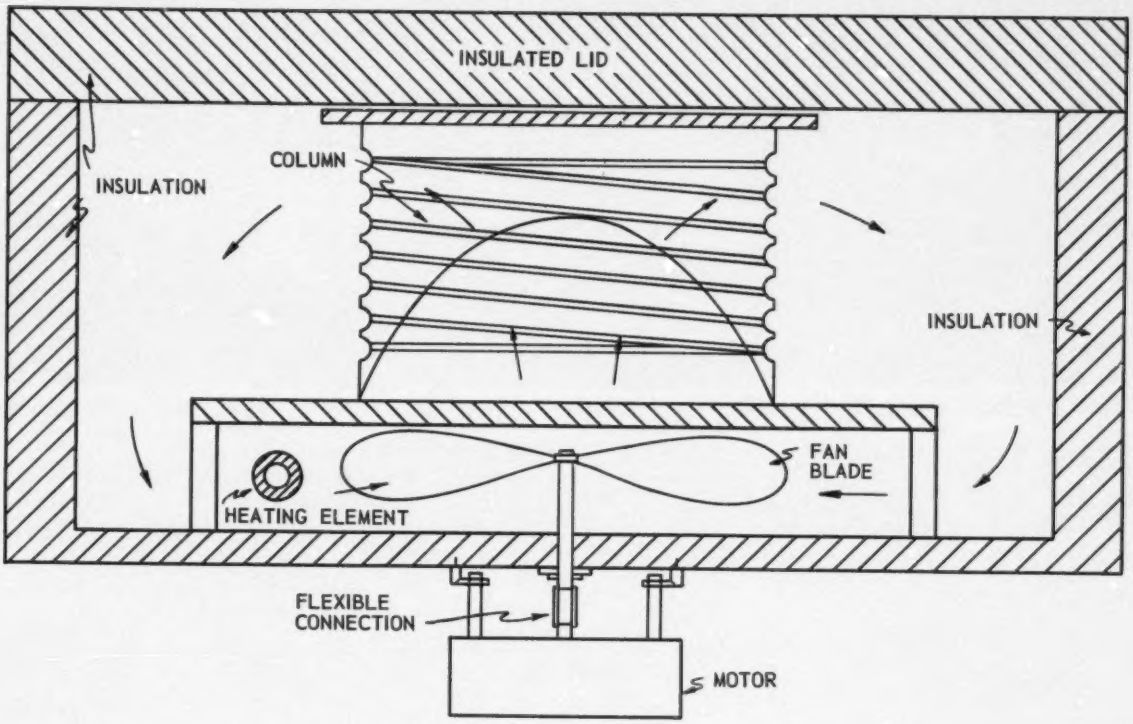

Figure 1. Temperature Controlled Column Compartment

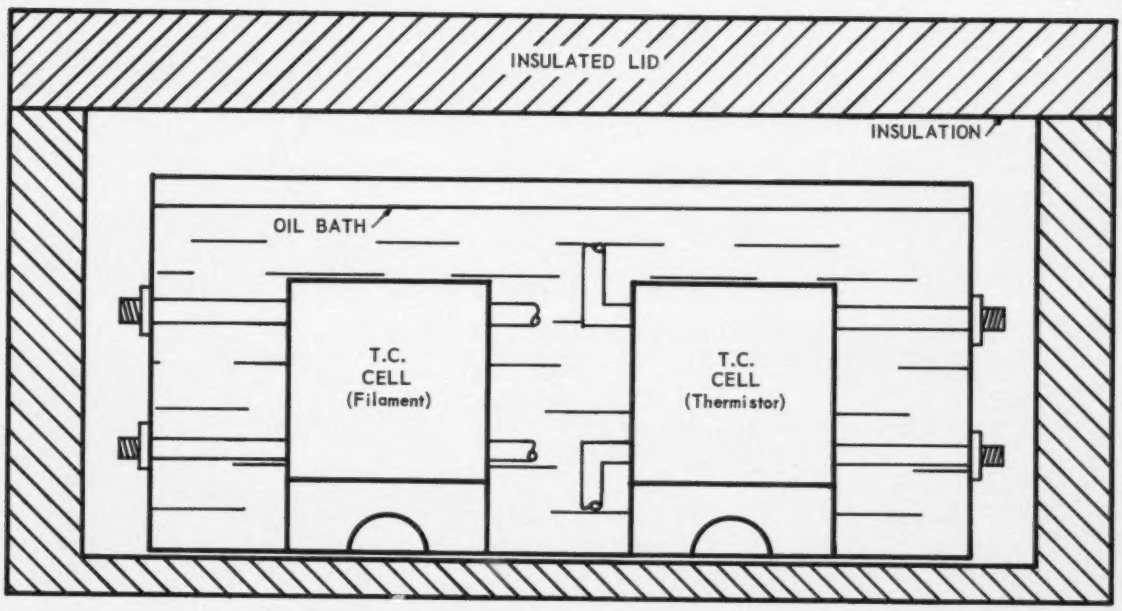

Figure 2. Temperature Controlled Detector Compartment

detector at a lower temperature (40°C) than the column oven. With the detector cell maintained at the lower temperature, the advantage of obtaining the higher sensitivity of the thermistor cell at low temperatures has been realized. A further improvement of temperature control is achieved by immersion of the detector in an oil bath which increases the base line stability.

The second detector, a filament-type of thermal conductivity cell, also shown in Figure 2, is provided with its separate power supply and bridge circuit. The purpose of the second unit is (a) to compare the sensitivities of the two types of thermal conductivity cells, and (b) to provide for two columns operating in series or in parallel.

Figure 3 is a schematic diagram of the thermal conductivity cell bridge circuit. The same bridge circuit is used with either filament or thermistor type of cell, except that in the latter case greater care is exercised to provide electrical shielding and to use special solder (Cd-Sn solder and untinned copper wire) for all connections. Temperature regulating circuits for both column and detector compartments are presented in Figure 4.

A Barber-Colman Wheelco recorder with a 0 - 1 mv range and a two second, full range, pen speed is used for recording the chromatogram.

(a) Power Supply and Improved Circuitry

The original power supply developed for use with the filament type thermal conductivity cell is shown in Figure 5. This power supply will deliver up to 200 ma DC at 15 volts with a long term drift of 5 mv/day. The noise level is less than 500 μv provided an ambient temperature of ± 3°C is maintained. This degree of regulation is more than

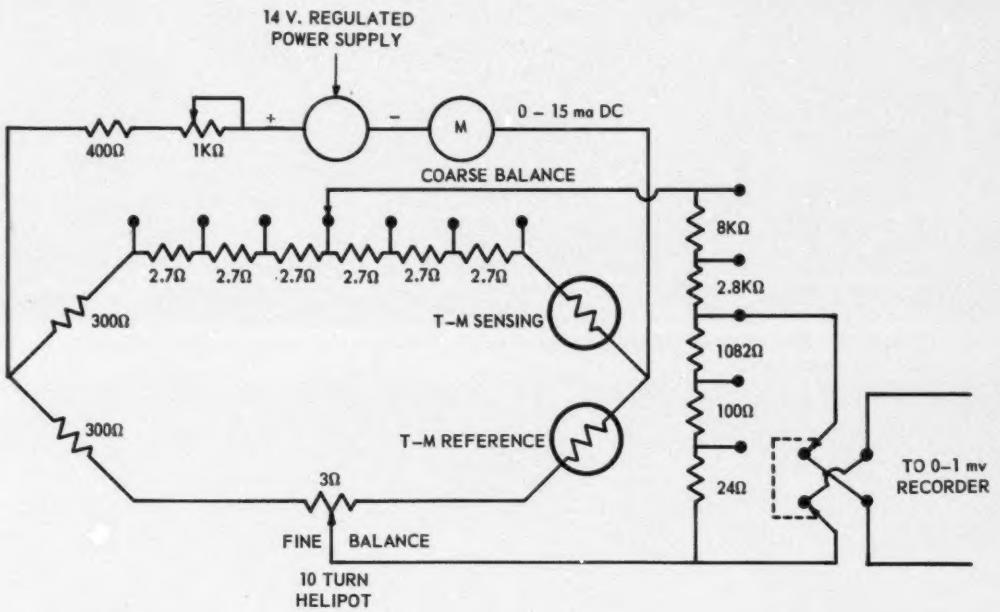

Figure 3. Thermal Conductivity Cell Bridge Circuit

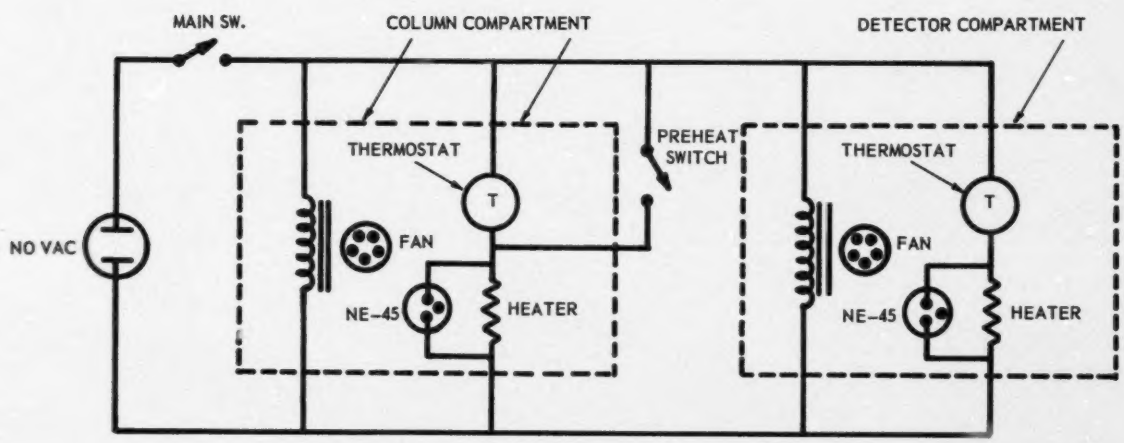

Figure 4. Gas Chromatograph Temperature Regulating Circuits

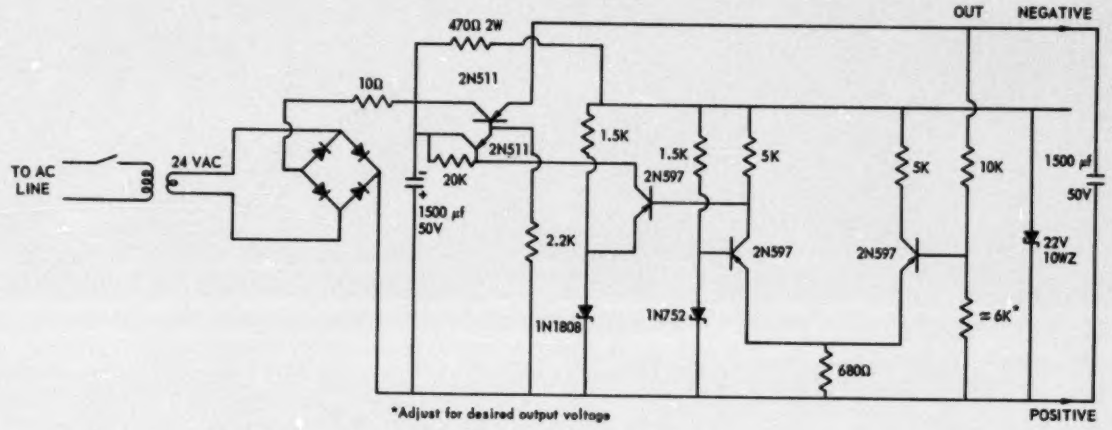

Figure 5. Regulated Power Supply for Filament Type Thermal Conductivity Cell

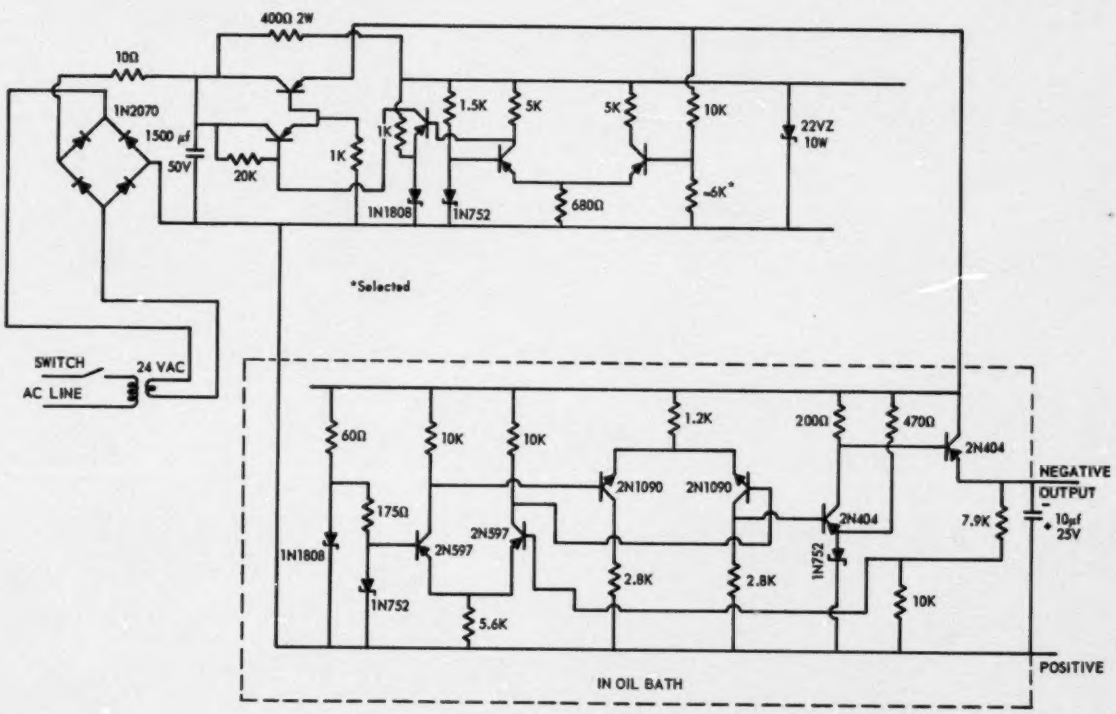

Figure 6. Regulated Power Supply for Thermistor Type Thermal Conductivity Cell

adequate for the power supply circuit stability, as this type of thermal conductivity cell is not highly sensitive to current fluctuations when operated on a bridge circuit.

The power supply for the thermistor type sensing cell, as shown in Figure 6, was found to require much better current regulation than was required for the filament type cell. This requirement is due to the characteristics of a thermistor which is much more temperature sensitive than the hot wire thermal conductivity cell. When the thermal conductivity cell was operated with the fine regulator circuit in an ambient temperature oil bath, the power supply shows the following drift rates: (a) one microvolt/^{o}C long term (ambient temperature dependent), and (b) less than three microvolts noise.

The power supply has proven to be more than adequate for the thermistor equipped analysis unit and the drift remaining is caused primarily by the temperature dependence of the thermistor cell. As mentioned above, placing of the thermistor cell in a regulated oil bath improved drift control.

A microvolt ammeter[1] has been operated in conjunction with the thermistor arrangement and it appears that this means of increasing chromatograph sensitivity will prove workable, provided adquate temperature regulation of the chromatograph components can be achieved. A 0 - 100 μv full-scale reading produces a tenfold increase in sensitivity of distinguishing chromatographic peaks without undue amount of drift. It is

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[1] Model 150 AR, manufactured by Keithley Instruments, Inc., Cleveland, Ohio.

recognized that thermocouple action becomes a problem at these low DC voltages and extreme care must be taken to prevent this effect from producing drift in the bridge circuit. Cadmium-tin solder and un-tinned copper wire were used to minimize this problem.

(b) Characteristics of the Experimental Gas Chromatograph

The chromatographic analysis unit was assembled especially for this project. The design and development had been worked out to a large measure under the research performed under another N.I.H. grant (25). The major departure of this analysis unit is in (a) the more refined temperature control, (b) separate temperature controls for column and thermal conductivity cell, and (c) ability to compare the performance from two cells concurrently or to operate a two-stage column for the resolution of a heterogeneous mixture of gases.

At the current stage of development, the unit still posseses several undesirable characteristics. Due to the high sensitivity, it is very critical that both sides of the bridge have exactly the same resistance. Installation of a variable resistor into one side of the bridge would solve this problem and also assist to compensate for resistance changes in the bridge circuit due to minor changes in operating pressure and cell temperature.

Another problem of the unit is temperature control in the column compartment when operating at elevated temperatures. Although fluctuations in the compartment temperature were observed to be less than 0.1^{o}C, the resulting changes in the carrier gas temperature produces a sinusoidal base line. The sinusoidal variation strongly suggests that the column compartment heater is responsible. At times, the base line variations

were larger than the analysis peaks. Operation of the analysis unit at room temperature avoided this problem, although it introduced serious problems with drift due to changes in room temperature.

The ultimate limiting factor in the unit was the thermistor detector. When used in the 0 - 1 mv circuit, its sensitivity permitted detection down to 500 p.p.m. H_2S which was one hundredth of the desired sensitivity of 5 p.p.m. Recommendations concerning the desirable characteristics for an improved unit in future work are discussed later, under Section VIII, "Suggestions for Future Work in this Field".

B. Gas Mixing Apparatus

To prepare component gases in a mixture of known concentration, an apparatus similar to that developed by Blanchard (26) was utilized with some modifications, as is shown in Figure 7. To determine the concentrations accurately, the apparatus is designed to make use of Dalton's Law of Partial Pressures. Two manometers are available for pressure determinations. One manometer is mercury-filled for those determinations requiring large changes in pressures and can be used only with nonreactive gases. The other manometer is filled with di-butyl phthalate because of its low vapor pressure, low density, and especially its low reactivity with the component gases.

(a) Outline of Operational Procedure

The operational procedure is presented herewith in condensed form for this report. To prepare a known mixture of gases, the first component is admitted through valve "X" to the previously evacuated flask "M", displacing the di-butyl phthalate to flask "$\overline{M}$". A portion of this gas is admitted into the evacuated system, including sample

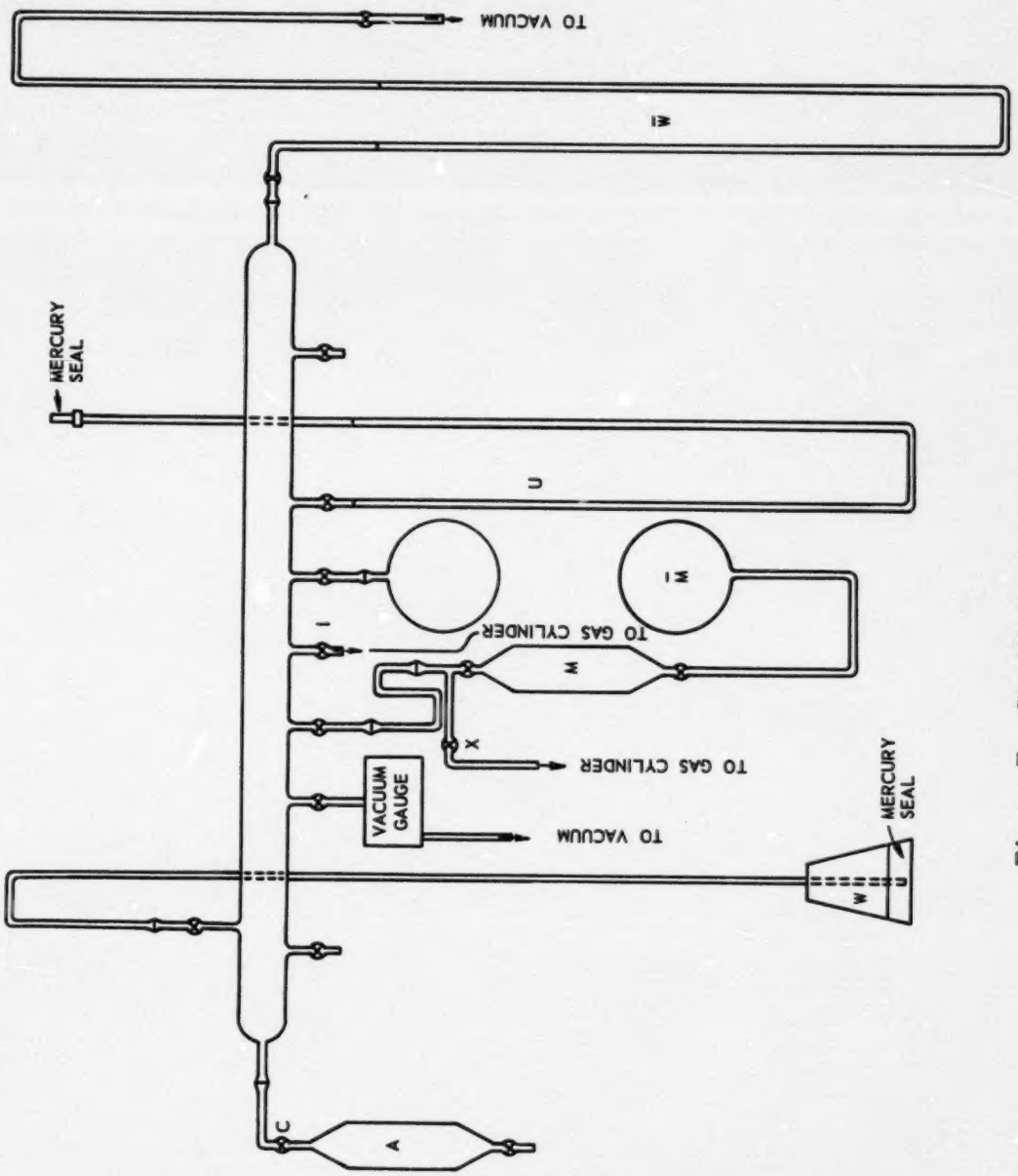

Figure 7. Gas Mixing Apparatus

flask "A". The di-butyl phthalate manometer "W" indicates the pressure of the sample, p_1, which is considerably less than atmospheric. Following this reading, valve "C" is closed and the system (other than flask "A") evacuated again to remove all traces of the first component. The second component is admitted through valve "I" until the gas bubbles through the mercury safety seal "W". Valve "C" is rapidly opened and closed several times until the pressure has been equalized between flask "A" and the rest of the system. The total pressure of the system, P, is indicated by the mercury manometer "U". This pressure is equal to the sum of the partial pressures of the two gaseous components, p_1 and p_2, in flask "A". The concentration of each component is found by the relation:

$$\text{Concentration of component "i"} = k \times \frac{p_1}{P}$$

where k is a constant relating the densities of mercury and di-butyl phthalate.

To prepare lower concentrations of the components or to add further components to the mixture, the system is evacuated, valve "C" is opened to reduce the mixture to a new total pressure, P_1, and valve "C" is closed. The procedure, as outlined above, is repeated with slight modifications depending on whether a dilution of the concentration or the addition of a third component is desired.

(b) Accuracy of Mixing Apparatus

The design and development of this unit was carefully directed toward an accuracy of sample composition of $\pm$ one per cent. To achieve this accuracy a vacuum of one millimeter of mercury is required. After overcoming some difficulties due to leakage and diffusion from rubber vacuum

tubing, it was possible to hold a vacuum of one mm of mercury or less for several hours, as corroborated by measurements with a McLeod vacuum gauge.

Although the di-butyl phthlate will not react appreciably with any of the component gases studied, the gases do dissolve to a limited extent in the phthalate. The search for a more suitable manometer liquid was not successful. However, the accuracy is not seriously impaired due to presaturation of the phthalate by bubbling the pure component gas through it and due to the brief contact time as well as small contact area between the liquid and gas phases.

Another consideration in the accuracy of this mixing device is the deviation from Dalton's Law of Partial Pressures due to the non-ideality of the component gases. This minor correction may be generally neglected due to the low working pressure of the system.

An evaluation of the sources of error and their magnitude, showing a theoretical average total error of one per cent, is presented in Appendix A.

IV. QUALITATIVE RESULTS WITH PACKED COLUMNS

A number of liquid partition solvents were evaluated to study the separation of components commonly associated with stack gases. The investigations included analyses of individual and synthetic mixtures of ammonia, methane, carbon monoxide, carbon dioxide, sulfur-containing compounds such as hydrogen sulfide, sulfur dioxide, methyl mercaptan and, of the oxides of nitrogen, nitrogen dioxide, nitrous oxide and nitric oxide. C-22 Firebrick was used as the solid packing material for all the columns. Studies were also conducted on the effect of temperature and flow rate on the separation of the component gases.

Each of the chromatographic columns were used with a thermistor cell and a 0 - 1 mv recorder. Helium was the carrier gas for all the analyses. The flow rate varied some depending upon the length of column, but was usually maintained at the rate of 50 mls per minute. Polyethylene tubing with a 1/4 in O.D. and 1/8 in I.D. was employed as the column, ranging from 6 to 28 ft in length. The partition packings were composed of 20 - 30% organic solvent coating on 70 - 80% solid support material by weight, using 28 - 48 mesh C-22 Firebrick. Fluoropak 80 [2] proved to be too hard to pack when coated and therefore was discarded as a possible support material.

The column liquids were weighed and dissolved in a suitable solvent, preferably ether, and thoroughly mixed with the firebrick. The mixture was air-dried, followed by oven drying at 100°C to assure good partitioning material.

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[2] Fluoropak 80, manufactured by the Fluorocarbon Company, 1206 E. Ash Ave., Fullerton, California.

Individual and synthetic mixture analyses were performed at the selected temperatures of 30°C, 60°C and 90°C. Initially, 30°C, 55°C, and 70°C had been selected as the temperature levels for column evaluation. However, the polyethylene tubing, specified to withstand a temperature to 80°C, melted at 70°C, which required changeover to Teflon tubing.

To evaluate column liquids and the effects of flow rate and temperature, the following parameters were determined: (a) specific retention volume, V_g^o, (b) number of theoretical plates, N, and (c) separation factor, R. The more precise definitions of these terms are presented in the glossary.

Specific retention volume is a measure of the power of a solvent to hold a specific component and is a function of column temperature for a given solvent and gas to be separated. The number of theoretical plates for a given column indicates the efficiency of separation and is a function of column temperature and pressure, flow rate, particle size, coating ratio, and column length, as well as the technique of packing. The separation factor is a combined function of retention volume and the number of theoretical plates. Therefore, R depends on the variables which affect the retention volume and the number of plates.

Some of the experimental results obtained with the various solvents are summarized in Tables I, II and III. Table I shows the specific retention volumes, characteristic of each component for a given partition liquid and temperature. Table II gives the same data for mixtures of these components.

It was observed that the retention volumes of components in mixtures are usually affected by the presence of other gases. In most mixtures, the retention volumes of the more weakly held components of a mixture

TABLE I. Specific Retention Volumes for Single Stack Gas Pollutants

Type of Column Length & % Coating by wt.		SO_2	CH_3SH	NO_2	CO_2	H_2S	NH_3	CH_4	N_2O
Silicone Oil 550									
27.4 ft	30°C	(*)	(*)	(*)	1.13 (32°)	5.47 (32°)	(*)	0.258 (32°)	(*)
30%	55°C	8.46 (55°)	18.9 (54°)	0.75 (55°)	0.86 (56°)	3.40 (56°)	N.S.	N.S.	(*)
	70°C	5.46 (71°)	N.S.	N.S.	N.S.	4.35 (72°)	N.S.	N.S.	(*)
Triton X-305									
6 ft	30°C	140 (34°)	50.5 (32°)	N.S.	3.88 (34°)	8.01 (32°)	N.S.	N.S.	(*)
30%	60°C	43.8 (62°)	15.6 (62°)	N.S.	N.S.	4.63 (62°)	N.S.	N.S.	(*)
Triton X-100									
6 ft	30°C	132 (31°)	42.8 (31°)	N.S.	1.25 (33°)	9.67 (32°)	N.S.	N.S.	(*)
30%	60°C	40.7 (61°)	45.6 (61°)	N.S.	N.S.	11.7 (60°)	N.S.	N.S.	(*)
Aerosol OT									
14 ft	30°C	25.3 (34°)	20.6 (31°)	N.S.	0.70 (34°)	4.10 (33°)	N.S.	N.S.	(*)
30%	60°C	13.5 (57°)	11.6 (56°)	N.S.	N.S.	2.71 (57°)	N.S.	N.S.	(*)
Triethanolamine									
4 ft	90°C	N.S.	56.3 (90°)	N.S.	N.S.	N.S.	25.2 (90°)	N.S.	N.S.
30%									
Triton N-57									
4 ft	30°C	(*)	65.9 (25°)	N.S.	1.15 (23°)	12.7 (25°)	N.S.	N.S.	1.69 (24°)
30%	60°C	43.2 (60°)	24.6 (60°)	N.S.	.950 (60°)	5.20 (60°)	N.S.	N.S.	1.12 (60°)
	90°C	21.1 (90°)	15.5 (90°)	N.S.	N.S.	4.20 (90°)	N.S.	N.S.	N.S.
Triton N-128									
4 ft	30°C	(*)	59.4 (27°)	N.S.	1.16 (28°)	14.4 (27°)	N.S.	N.S.	1.38 (27°)
31.15%	60°C	59.3 (60°)	25.6 (60°)	N.S.	N.S.	7.32 (60°)	N.S.	N.S.	1.12 (60°)
	90°C	22.5 (90°)	13.6 (90°)	N.S.	N.S.	4.42 (90°)	N.S.	N.S.	N.S.
Silica Gel									
1 ft	30°C	(**)	(**)	N.S.	C.S.	C.S.	(**)	N.S.	C.S.
100%	60°C	(**)	(**)	N.S.	24.0 (60°)	101 (60°)	(**)	N.S.	20.2 (60°)
	90°C	168 (90°)	(**)	N.S.	8.86 (90°)	31.7 (90°)	(**)	N.S.	7.66 (90°)
Di-butyl phthalate									
4 ft	30°C	75.9 (25°)	66.2 (28°)	I.S.	1.92 (23°)	10.6 (27°)	N.S.	N.S.	2.48 (25°)
29.17%	60°C	25.7 (60°)	27.9 (60°)	N.S.	I.S.	5.78 (60°)	N.S.	N.S.	1.49 (60°)
	90°C	11.9 (90°)	15.3 (90°)	N.S.	0.98 (90°)	(*)	N.S.	N.S.	.974 (90°)

C.S. Complete Separation
I.S. Incomplete Separation
N.S. No Separtion

(*) Not determined
(**) Chemical reaction between components

TABLE II. Specific Retention Volumes for Various Mixtures of Stack Gas Pollutants

	Aerosol OT			Triton X-305	
	34°C	57°C		40°C	70°C
H_2S + CH_3SH	4.04 19.5	2.70 11.6	H_2S + CH_3SH	3.97 16.3	2.92 10.1
CH_3SH + SO_2	19.6 45.2	11.7 17.9	H_2S + SO_2	4.07 44.7	2.68 19.7
H_2S + CH_3SH + SO_2	4.03 19.3 45.2	2.73 11.5 17.3	CH_3SH + SO_2	16.4 45.1	10.4 20.1
Pure H_2S	4.10	2.71	H_2S + CH_3SH + SO_2	4.20 16.6 45.3	2.44 9.77 19.1
Pure CH_3SH	20.6	11.6			
Pure SO_2	25.3	13.5	Pure H_2S	3.78	5.72
			Pure CH_3SH	16.3	9.89
			Pure SO_2	44.4	20.9

TABLE III

Theoretical Plate Number and Separation Factor for Stack Gas Components on Different Column Solvents

Column Coating % by Wt.	Temp. °C	H_2S		CH_3SH		SO_2		CO_2		NH_3		NO_2		N_2O	
		N	R	N	R	N	R	N	R	N	R	N	R	N	R
30% Silicone Oil 550 27.4 ft	55	711	4.22	612	8.16	833	6.98	229	0.82	N.S.	N.S.	260	.85	(*)	(*)
	70	190	2.29	N.S.	N.S.	167	2.53	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	(*)	(*)
30% Triton X-100 6 ft	30	169	2.51	254	5.56	170	5.96	85.1	0.54	N.S.	N.S.	N.S.	N.S.	(*)	(*)
	60	119	1.44	155	3.42	268	5.62	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	(*)	(*)
30% Triton X-305 6 ft	30	80	2.08	125	4.21	254	7.03	19.1	0.34	N.S.	N.S.	N.S.	N.S.	(*)	(*)
	60	64	1.30	111	3.11	184	5.18	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	(*)	(*)
30% Aérosol OT 14 ft	30	95	1.60	90	3.53	44	2.57	54.4	0.50	N.S.	N.S.	N.S.	N.S.	(*)	(*)
	60	78	1.08	81	2.41	65	2.52	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	(*)	(*)
30% Triethanolamine 4 ft	90	N.S.	N.S.	80.6	3.53	N.S.	N.S.	N.S.	N.S.	49.5	2.36	N.S.	N.S.	N.S.	N.S.
30% Triton N-57 4 ft	30	141	3.92	165	5.64	(*)	(*)	122	1.07	N.S.	N.S.	N.S.	N.S.	88.3	1.05
	60	134	1.38	154	4.53	137	4.73	70.3	0.43	N.S.	N.S.	N.S.	N.S.	78.2	0.53
	90	66.8	1.27	82.4	2.67	62.5	2.82	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
31.15% Triton N-128 4 ft	30	112	3.18	226	0.60	(*)	(*)	75.7	0.828	N.S.	N.S.	N.S.	N.S.	132	0.933
	60	119	1.26	183	0.76	183	0.42	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	67.2	0.40
	90	146	1.78	154	3.10	158	4.06	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
100% Silica Gel 1 ft	30	(*)	(*)	(**)	(**)	(**)	(**)	(*)	(*)	(**)	(**)	N.S.	N.S.	(*)	(*)
	60	90.0	3.61	(**)	(**)	(**)	(**)	102	1.86	(**)	(**)	N.S.	N.S.	96.2	1.71
	90	59.2	1.93	(**)	(**)	43.2	2.85	65.0	0.949	(**)	(**)	N.S.	N.S.	53.4	0.883
29.17% Di-butyl phthalate 4 ft	30	314	5.00	405	8.90	419	9.24	284	1.88	N.S.	N.S.	I.S.	I.S.	262	2.21
	60	681	4.88	431	8.02	300	6.58	I.S.	I.S.	N.S.	N.S.	N.S.	N.S.	233	1.19
	90	I.S.	I.S.	393	6.04	174	4.08	194	0.638	N.S.	N.S.	N.S.	N.S.	133	0.652

I.S. Incomplete separation
N.S. No separation
(*) Not determined
(**) Chemical reaction between components

decreased, while those of the more strongly adsorbed components increased. This phenomenon requires further study for positive identification of components in mixtures. Derivations of a functional relationship of the effect of mixture components on each other during chromatographic resolution would be extremely useful in the analysis of stack gas.

Mixtures of hydrogen sulfide and sulfur dioxide were found to react to form elemental sulfur in the syringe prior to injection. It was discovered later that a mixture - not producing any precipitate of sulfur - consisting of one part hydrogen sulfide, two parts methyl mercaptan and two parts sulfur dioxide by volume yields separate peaks for each component. With this mixture no visible reaction occurred in the syringe, although this is not complete evidence that no reaction takes place between these gases in the syringe.

As the result of considerable experimental work and analysis, Table III provides a summary of the calculated number of theoretical plates, N, and the separation factor, R, for each component on each of the columns. These parameters, N and R, are characteristic of the given column and component combinations when the same flow rate and column temperature are maintained. As both of these parameters are directly affected by column length and since these columns are not necessarily of optimum length, a direct comparison of their values for a given gas on various partition liquids is not possible. However, the values are valid for a comparison of the particular columns as listed in Table III.

The separations of hydrogen sulfide, sulfur dioxide, and methyl mercaptan, using Triton X-100 and Triton X-305, confirm the findings of Adams and his co-workers (8). The relative retention volumes of hydrogen

sulfide and sulfur dioxide (using methyl mercaptan as the standard solute) produced the following comparison data at 30°C:

Substance	Triton X-100		Triton X-305	
	Data by Adams	Data from Table I	Data by Adams	Data from Table I
H_2S	0.27	0.23	0.16	0.16
SO_2	2.93	3.07	3.45	2.78

Results achieved with both partition liquids show a definite agreement for hydrogen sulfide, while the results for sulfur dioxide show some deviation. Throughout most of this investigation, the chromatographic response to sulfur dioxide shows permanent adsorption and some tailing of the peak. These phenomena create variation in retention volumes and thereby influence the above comparison data to some degree. Also, the evaluation of Silicone Oil 550 for the separation of hydrogen sulfide confirms the results presented elsewhere (27).

Irreversible adsorption, as previously defined (27), was observed with sulfur dioxide using Triton X-100, Triton X-305, Silicone Oil 550 and Aerosol OT, with the Aerosol OT column showing the least adsorption. The column materials adsorb a portion of the sample gas irreversibly. Complete saturation of the column with sample gas is necessary before a complete sample can emerge from the column. Under continuous analytical work, the columns remained saturated for periods of approximately two weeks with a constant helium flow of approximately 50 mls per minute. In addition to sulfur dioxide adsorption, the Silicone Oil 550 column also adsorbed

hydrogen sulfide, although to a lesser degree than SO_2 for the same column. This effect could also be removed by presaturation of the column.

Incomplete separation of carbon dioxide was observed with Silicone Oil 550, Aerosol OT, Triton X-100, and Triton X-305. Longer column lengths would improve these separations, although it may not always yield complete separation.

Chromatographic separation of nitrogen dioxide was not possible with the particular partition solvents described. Only incomplete separations with Silicone Oil 550 and di-butyl phthalate were obtained. Sample introduction, using the syringe needle technique, proved to be a difficult problem in this instance. The reddish-brown color of the nitrogen dioxide gas usually disappeared before the sample could be injected and no visible peaks were produced. The disappearance of the characteristic color is believed to be a reaction of the nitrogen dioxide with the syringe lubricating grease, or due to decomposition of the gas.

Methane was not separated successfully by any of the partition columns at the lengths investigated, although partial separation was obtained on the Silicone Oil 550 column.

Some experimental work was conducted to study the effect of flow rate on column efficiency and separation. The effect of flow rate on the number of theoretical plates, N, of a Triton X-100 partition column is shown in Figure 8. This study of column efficiency from an air - SO_2 mixture separation is based on four different flow rates. It appears that increasing the flow rate decreases the column efficiency. This observed effect may be partially due to the decrease in time permitted for attainment of absorption equilibria. The effect of flow rate on the separation factor, R,

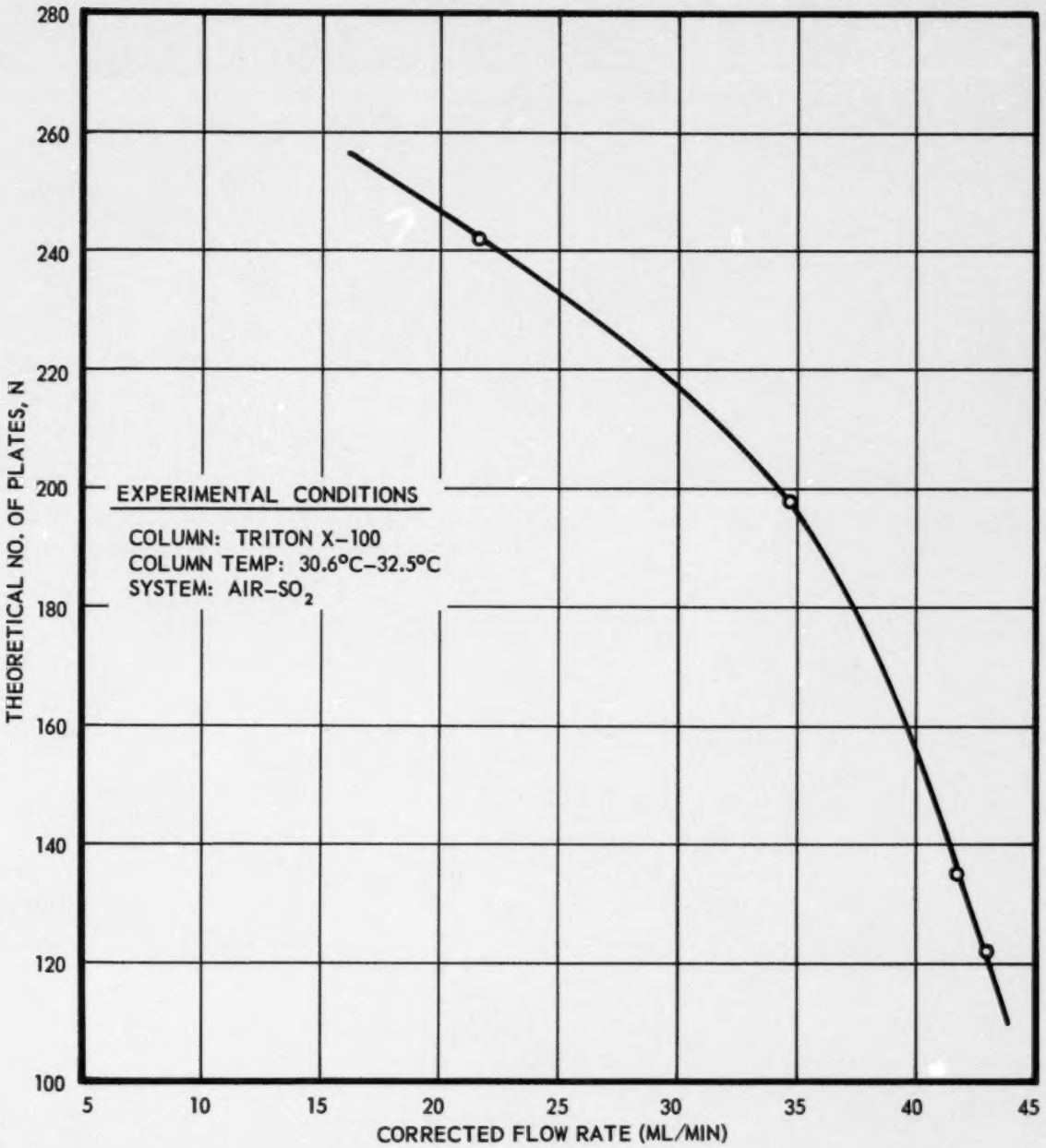


Figure 8. Dependence of Theoretical Number of Plates Upon Flow Rate

for the same experimental runs is shown in Figure 9. The decrease of separation with increasing flow rate may be explained on the same basis of incomplete absorption equilibria.

The effect of temperature on retention volume is shown in Figures 10 and 11. It is seen that increasing the temperature usually decreases the retention volume. This effect is due to the higher vapor pressure of gases at elevated temperatures, which decreases the ability of the coating fluid to hold the component. Quantitatively, this represents a lowering of the absorption equilibrium constant. From theoretical considerations, a straight line relation is expected if the logarithm of specific retention volume, V_g^o, is plotted against the reciprocal of absolute column temperature. The plots are useful for correcting specific retention volumes for discrete temperatures and for their prediction at various other temperatures.

Although time did not permit the optimization of the various columns, this information would be very valuable for continuous monitoring analyses. The logical procedure to be followed would be:

(a) Knowing the gases to be analyzed, a suitable coating liquid would be selected,

(b) A support material and mesh range would be chosen so as to minimize tailing, permit ease of column packing and provide a low pressure drop across the column,

(c) Column length would be determined such that satisfactory separation would be obtained between all components (separation factor greater than 1.5).

(d) Flow rate and operating temperature (if appropriate, "programmed" temperature) would be selected for minimum analysis time and least amount of tailing.

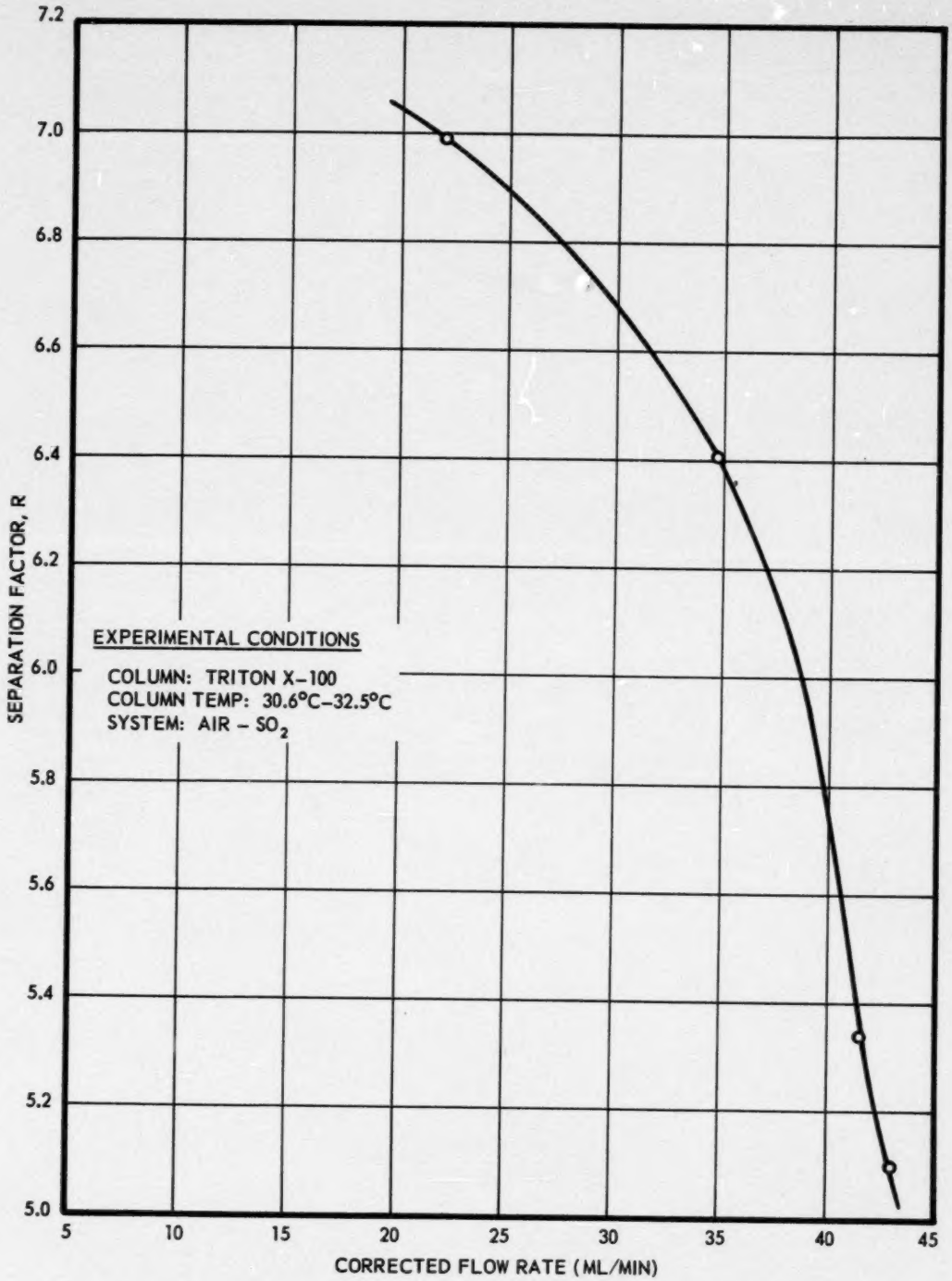
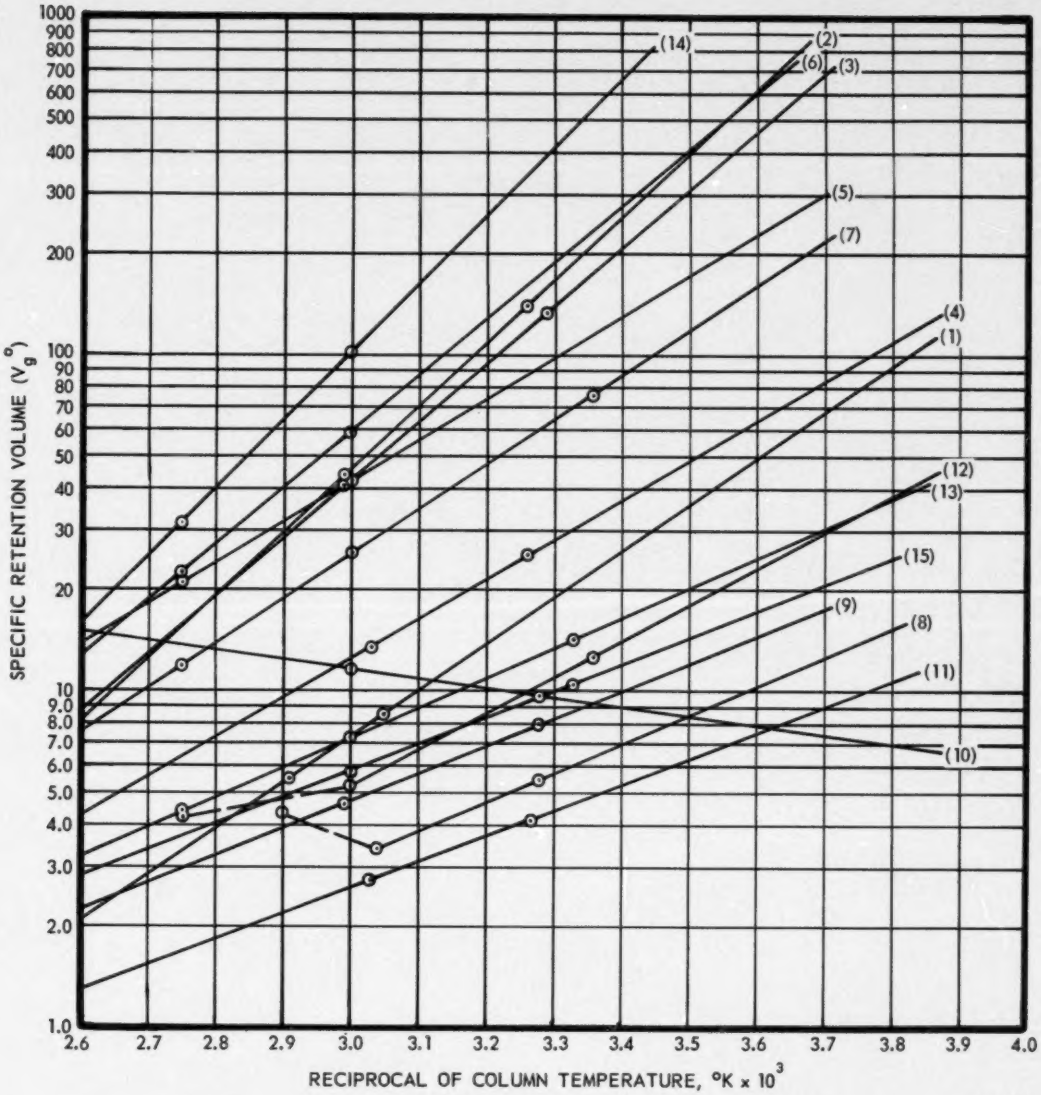
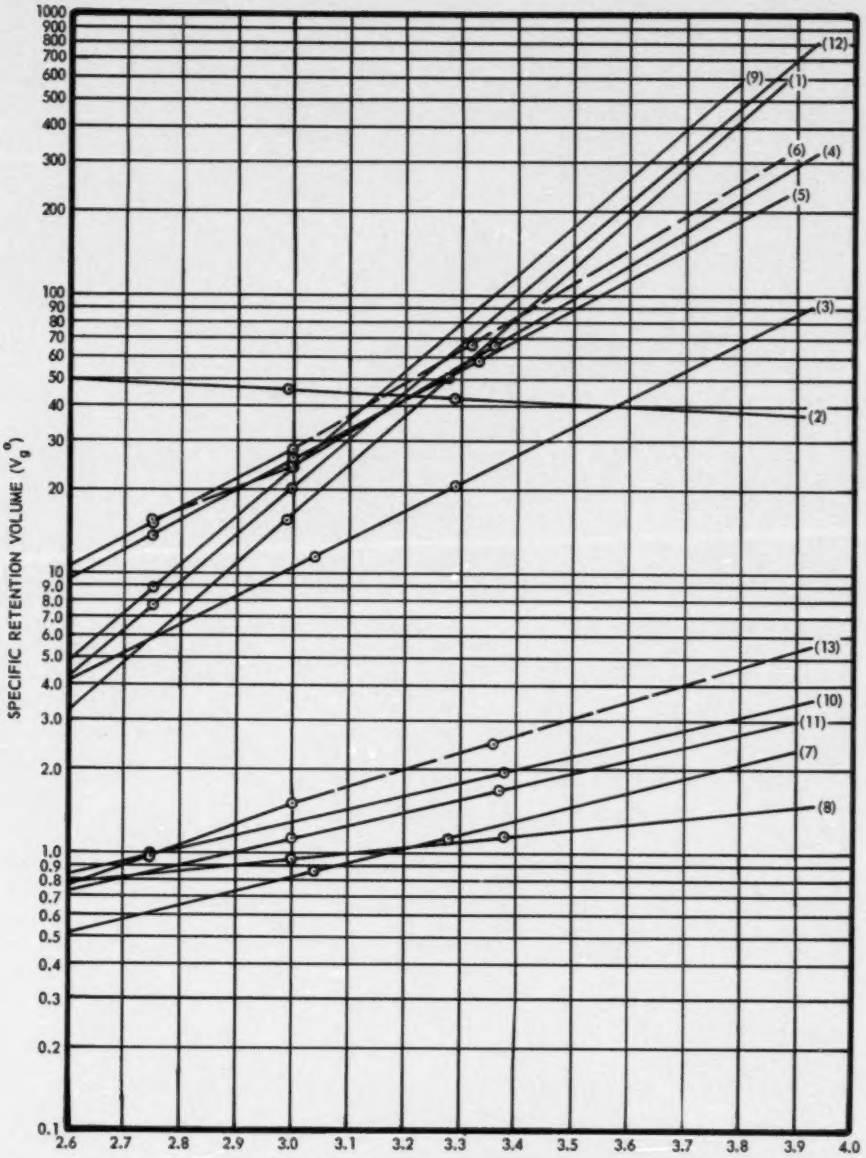


Figure 9. Dependence of Separation Factor Upon Flow Rate



(1) SO_2 ON SILICONE OIL 550
(2) SO_2 ON TRITON X-305
(3) SO_2 ON TRITON X-100
(4) SO_2 ON AEROSOL OT
(5) SO_2 ON TRITON N-57
(6) SO_2 ON TRITON N-128
(7) SO_2 ON DIBUTYL PHTHALATE
(8) H_2S ON SILICONE OIL 550
(9) H_2S ON TRITON X-305
(10) H_2S ON TRITON S-100
(11) H_2S ON AEROSOL OT
(12) H_2S ON TRITON N-57
(13) H_2S ON TRITON N-128
(14) H_2S ON SILICA GEL
(15) H_2S ON DIBUTYL PHTHALATE

Figure 10. Effect of Temperature Upon Specific Retention Volume



(1) CH_3SH ON TRITON X-305
(2) CH_3SH ON TRITON X-100
(3) CH_3SH ON AEROSOL OT
(4) CH_3SH ON TRITON N-57
(5) CH_3SH ON TRITON N-128
(6) CH_3SH ON DIBUTYL PHTHALATE
(7) CO_2 ON SILICONE OIL 550
(8) CO_2 ON TRITON N-57
(9) CO_2 ON SILICA GEL
(10) CO_2 ON DIBUTYL PHTHALATE
(11) N_2O ON TRITON N-57
(12) N_2O ON SILICA GEL
(13) N_2O ON DIBUTYL PHTHALATE

Figure 11. Effect of Temperature Upon Specific Retention Volume

Each column and set of operating conditions must be calibrated with known samples of the gases to obtain the retention volumes which make the analysis qualitative. This initial calibration is necessary as it is impossible to coat and pack the column materials reproducibly. The preparation of new columns, or their recalibration, will only be necessary infrequently when columns are coated with high molecular weight organic liquids. The long column life is due to the low blow-off of the organic coating material, providing a useful column for periods exceeding a year.

In devising a particular analysis, it may be impossible to find a single coating liquid which will satisfactorily separate all the desired components. In such a case, it is possible to select two columns which will effect the desired separation if connected in series as shown in Figure 12. For two-stage operation, the base line is adjusted to the middle of the recorder chart and the sensitivity is reduced one-half in order to record both the positive and negative peaks.

As an example, suppose a mixture of gases A, B, C and D is analyzed by the dual column arrangement presented in Figure 12. The resulting chromatogram is shown in Figure 13. Gases A and B are not separated and therefore pass through Column I together; but gases C and D are resolved. While the components are passing through one side of the detector, pure carrier gas is passing through the other side which acts as the reference side. Gases A and B are then separated in Column II, followed by the somewhat diffused peaks of C and D. This arrangement is particularly useful where some of the components are irreversibly absorbed by one of the columns. In this example, C and D could have been absorbed by Column II, while the analysis would still have been complete.

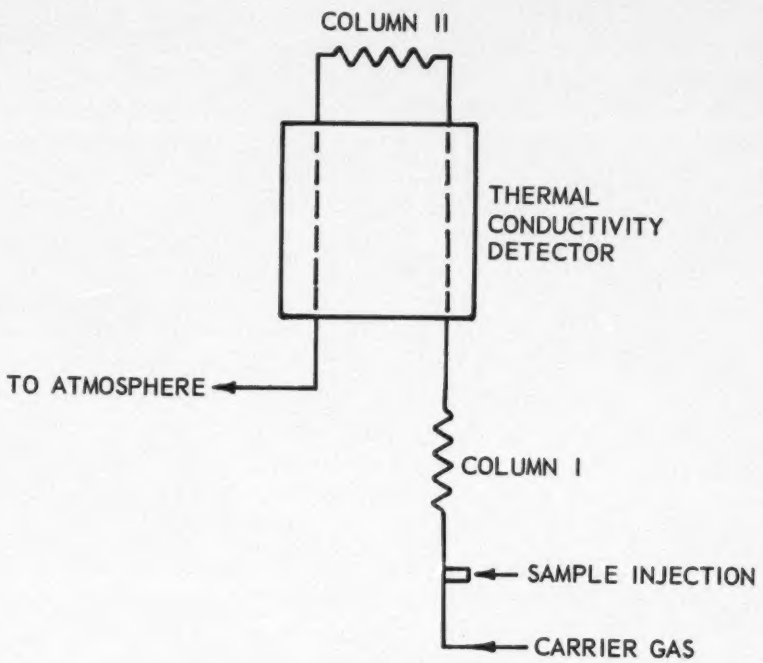


Figure 12. Arrangement for Columns in Series

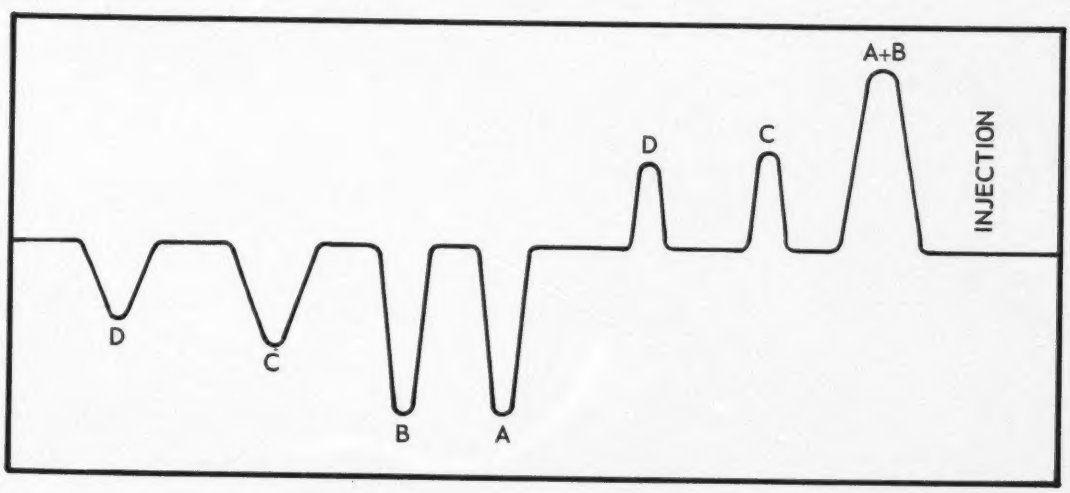


Figure 13. Chromatogram from Columns in Series

V. QUANTITATIVE RESULTS WITH PACKED COLUMNS

A. Methods of Quantitative Calibration

Due to the existence of a number of types of detectors, individual detectors of the same type, types of columns, individual columns of the same type, operating conditions, and characteristics of the gases to be analyzed, it is necessary to standardize a chromatographic analysis by quantitative calibration of the system. The same operating conditions of the calibration should then be maintained in all subsequent analyses. Upon installation of a new column, different types of detector or any change of operating conditions, the calibration must be repeated.

The most accurate method for calibration is based on the peak area. In this method, samples of various concentrations of each component are analyzed and the resulting peak areas are determined by an automatic integrator or a manual planimeter. The areas are then plotted against the concentration of the component.

In those instances where the characteristics of the gases are very similar, the concentration may be obtained directly by dividing the peak area of the component of interest by the sum of all the peak areas of the chromatogram. However, in cases where this method is not applicable, the previously described plot is necessary.

Whenever tailing is a problem, it may be advantageous to use tangent areas, where the tangent area is the area bounded by the tangents to the sides of the peak and the baseline. This method, however, requires manual determination of area and a calibration plot.

The other method of calibration is based on peak height. Since the peak width is essentially constant as determined by the column and operating

conditions, it is possible to obtain very good correlation between concentration and peak height, as reported elsewhere (25), provided conditions are held constant.

With both the peak area and the peak height methods of calibration, it is possible to analyze various sizes of samples of a known gas concentration and to plot the resulting peak height, or area, versus the calculated amount of the pure component. This calibration technique eliminates the need for having several cylinders of standard gases on hand. However, this procedure may introduce some error due to the fact that more than one size of syringe, or other injection device, may be required to obtain the desired range of peaks.

B. Gases Studied

All quantative work was performed with H_2S, SO_2 and CH_3SH. These gases[3] were acquired in 99% or higher, purity, in analyzed mixtures with nitrogen, and in certified mixtures with each other.

C. Gas Mixtures Compounded with the Gas Mixing Apparatus

The gas mixing apparatus was employed to make known mixtures of H_2S in nitrogen from the pure gas to supplement the data obtained from one, three and five per cent certified H_2S mixtures. The mixtures prepared in the laboratory employed nitrogen as the diluent, as did the certified standard gases.

However, the mixtures prepared by the mixing apparatus produced chromatographic peaks which were from 1.75 to 2.25 times as large as those obtained with the standard mixtures. Considerable work with wet chemical

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[3] Available from The Matheson Company, East Rutherford, New Jersey.

analyses (28), following the chromatographic analysis of both types of mixtures, confirmed the magnitude of error in mixture preparation.

To investigate the accuracy of the mixing apparatus, various samples of CO_2 were prepared and their chromatographic analyses agreed with those obtained in previous work (25)(27) in which accurately known amounts of CO_2 were injected. It is of significance that the earlier work did not employ the gas mixing device.

The disagreement of values obtained from the two methods of H_2S mixture preparation considerably reduced the progress of the quantitative analysis work and the problem was never satisfactorily resolved.

D. Difficulties Encountered in Quantitative Work

The original proposal for this research grant specified the construction of a laboratory model chromatographic analyzer. Such a unit was designed and constructed at a savings of about $2,000 as compared to the initial cost of a commercial unit. This analysis unit proved to be entirely satisfactory for the qualitative phase of this project, but it was found to be inadequate for quantitative work.

The major problems, attributable to the unit, included: (a) base line drift due to insufficient insulation, (b) sinusoidal base line pattern at elevated temperatures due to poor thermostating, and (c) unstable base line due to corrosion in the detector by the sulfurous gases, although all possible precautions were taken and the detector cell frequently flushed out and cleaned.

The sinusoidal base line pattern tended to invalidate any quantitative work at elevated temperatures, and made it necessary to continue the studies at room temperature. The room temperature changes caused some base

line drift and also caused some differences in day-to-day results.

During those days when the unit temperature was almost constant ($\pm$ 1°C), the results were still not highly reproducible. This difficulty was evidently due to the syringe method of sample injection.

E. Quantitative Results Obtained

The lower limit of quantitative detection of H_2S, SO_2 and CH_3SH for the unit, when employing non-optimized columns, was found to be about 500 p.p.m. This detection limit could undoubtedly have been lowered to about 100 p.p.m. using optimized columns which would give sharper peaks. However, time did not permit undertaking of this refinement.

Due to the previously discussed difficulties encountered with the unit, some of the quantitative data obtained had some scatter. The following curves are presented to summarize some of the results obtained.

Figure 14 is a plot of peak height versus H_2S concentration for three different sizes of samples injected. This data was obtained on a 1/4 in O.D., 1/8 in I.D., ten ft long, 30% di-butyl phthalate on C-22 Firebrick column, operated at room temperature (approximately 27°C). A thermistor-type thermal conductivity cell was used as the detector, also maintained at room temperature, with a cell current of 15 milliamperes and a helium flow rate of about 50 ml/min.

Figure 15 is a plot of peak height versus amount of CH_3SH, obtained with various sizes of samples of a certified mixture of 3.14% CH_3SH in nitrogen. This data was obtained from a similar di-butyl phthalate column two feet long, with the same detector and operating conditions. Results for SO_2 on the same two ft di-butyl phthalate column are presented in Figure 16. The SO_2 results were obtained by analyzing various sample sizes (0.1 to 0.5 ml) of a certified mixture of 5.37% SO_2 in nitrogen.

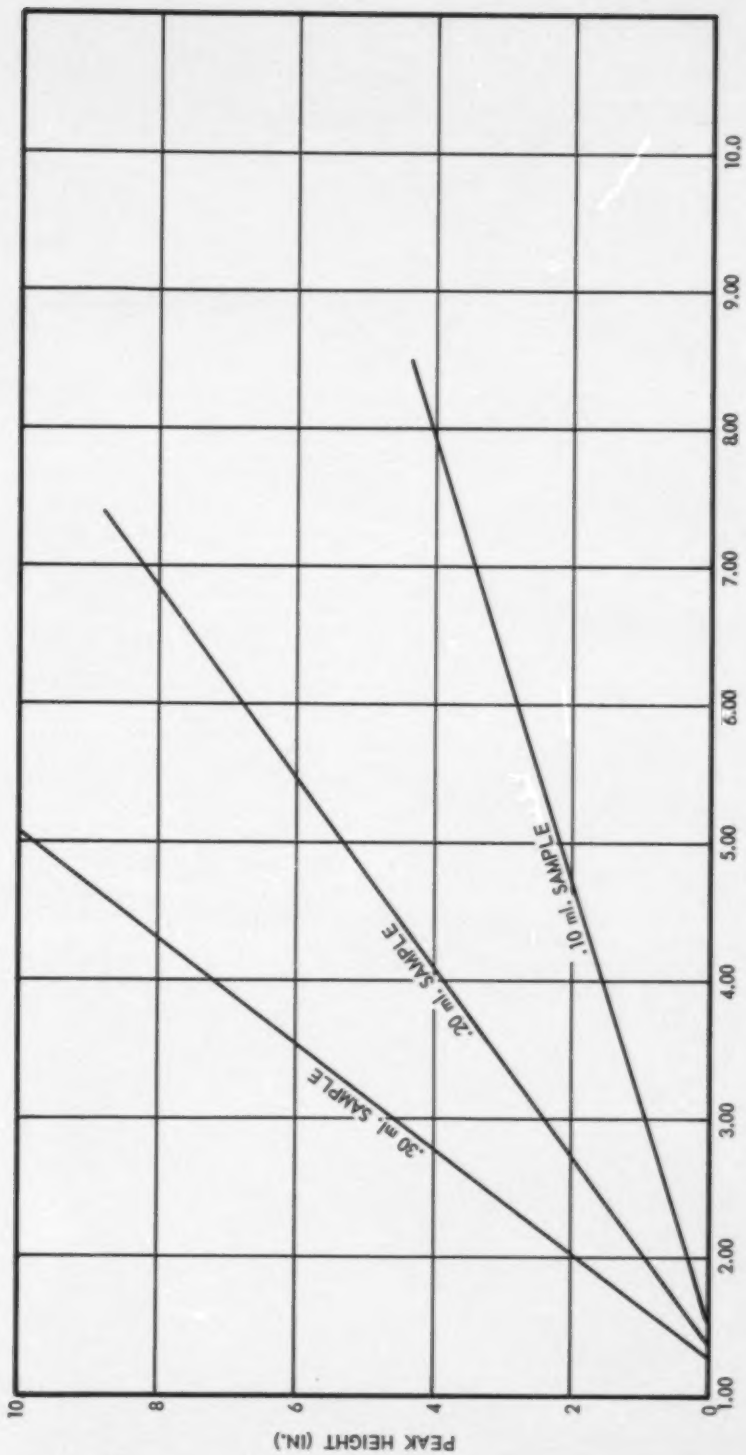

Figure 14. Peak Height Versus Concentration of H_2S

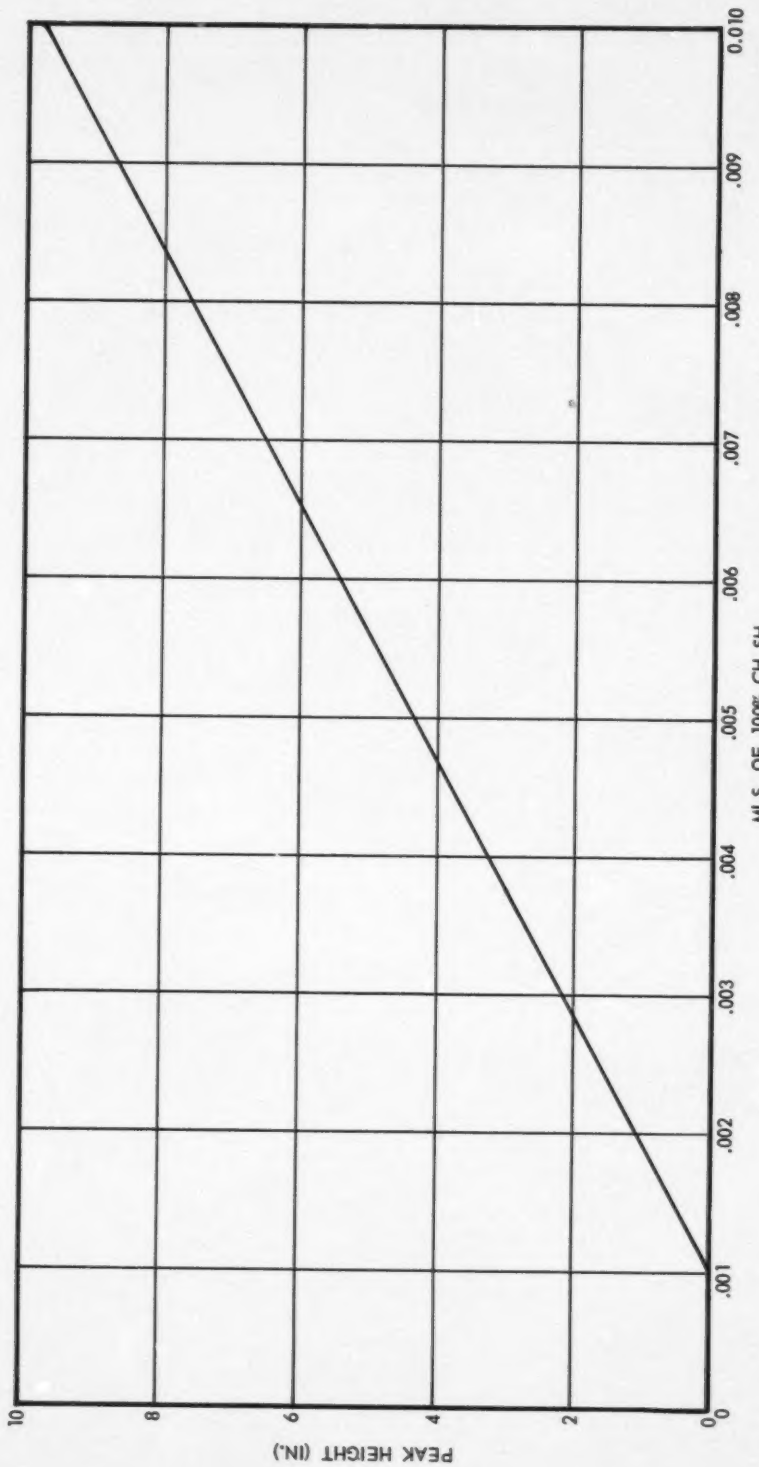

Figure 15. Peak Height Versus Volume of CH_3SH

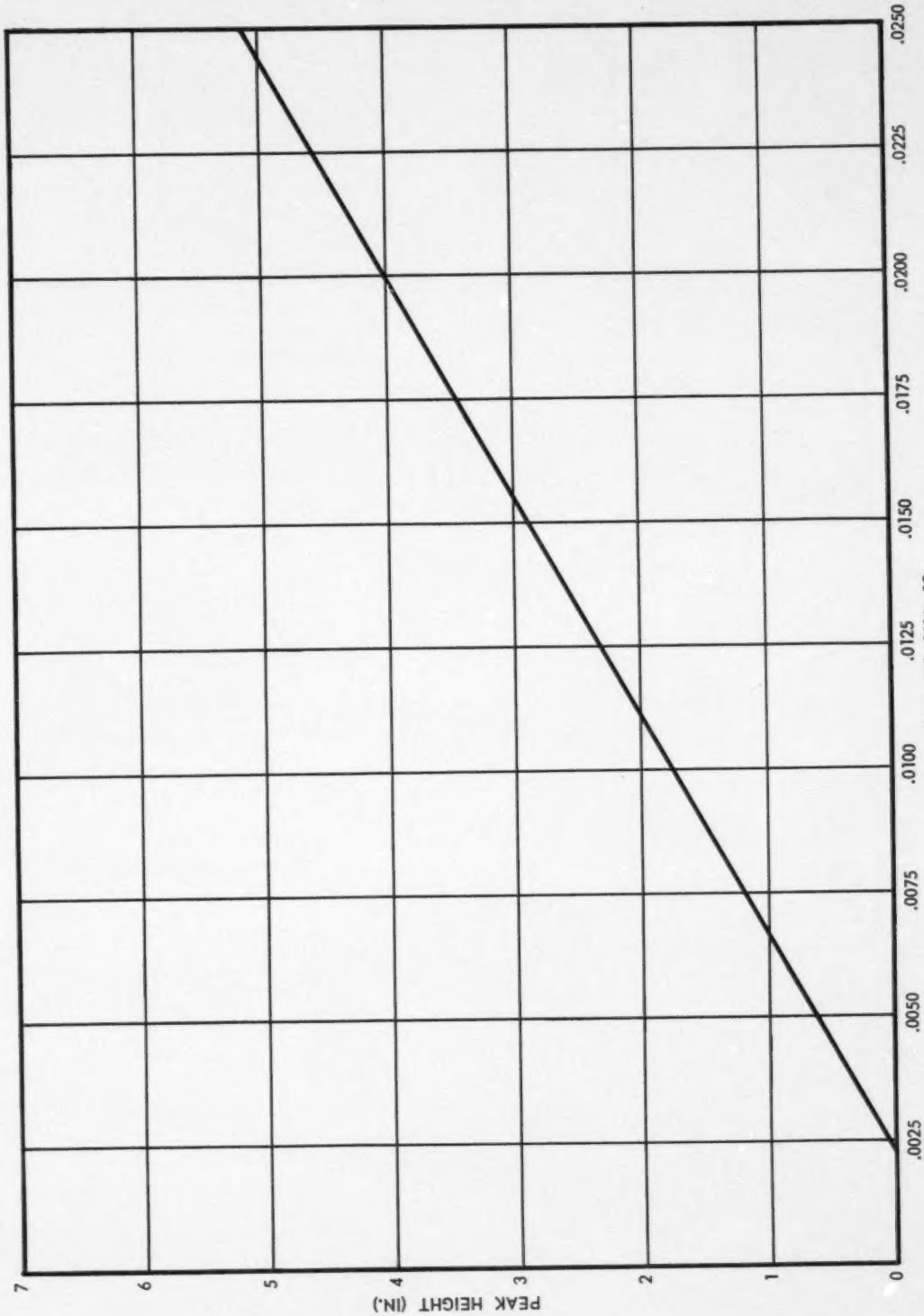

Figure 16. Peak Height Versus Volume of SO_2

VI. EXPERIMENTAL RESULTS WITH CAPILLARY COLUMNS

A. Introduction

The separation of gases on packed columns takes place in a system of channels and cavities between the individual particles of packing material. The system may be considered as one of interlinked capillaries which achieves the separation. A more uniform liquid film is obtained in a capillary column than is possible in a packed column.

The major disadvantages of the capillary column are the criticality of the coating procedure and the requirement for very small gas samples. These disadvantages are partially offset by greater column uniformity, shorter diffusion time, elimination of undesirable adsorption by the solid support and lower resistance to gas flow, as compared to packed columns.

The use of 0.2 mm diameter columns in gas chromatography was originally suggested by Martin (29). The first theoretical and practical considerations of coated, tubular columns were described by Golay (30) and Burrows (31). Nylon tubing columns of 0.01 and 0.02 in I.D. were used by Scott (32) to yield high efficiencies. Columns of 0.02 in and 0.034 in diameter have been found to yield efficiencies up to 250,000 theoretical plates in the separation of hydrocarbons. Zlatkis (33) also prepared a nylon column, one mile in length with a diameter of 0.066 in, and reported an efficiency of one million theoretical plates, which is equivalent to 190 plates per foot.

Definite advantages of the capillary column over the packed column have been predicted when applied to theory development, separation of extremely small amounts of mixtures, separation of substances of high molecular weight, or low vapor pressure, without the need of resorting to very high temperatures, or temperature programming (34). Considering these advantages

and the early reported successes of capillary columns, they promised to be beneficial in the analysis of stack gases and, therefore, were evaluated during the first year of this research project.

B. Coating of Columns

Two coating liquids, 10% (by vol.) squalane in chloroform and 7.2% (by vol.) Triton X-100 in chloroform, were studied.

The column was partially filled with the coating liquid and helium was applied at sufficient pressure to force the liquid to pass through the "spaghetti", or column. The flow rate was adjusted to a linear velocity inside the column, not to exceed 10 cm/sec., which for 0.075 cm I.D. tubing corresponds to 9 - 10 ml/min. The column was flushed with the gas until the chloroform completely evaporated.

C. Columns Studied

All columns were 1/16 in O.D. nylon, with a volumetrically determined I.D. of 0.0752 cm. The following columns were prepared:

(a) 200 ft squalane, 0.1992 total gm coating liquid

(b) 425 ft Triton X-100, 0.3852 total gm coating liquid

(c) 275 ft Triton X-100, 0.2373 total gm coating liquid

(d) a combination of (b) and (c), providing a 700 ft Triton X-100 series column.

D. Results Obtained

The separations achieved for various individual stack gas components and mixtures are summarized in Table IV.

No separation of H_2S from air was obtained using the squalane column. Incomplete separation with the 425 ft Triton X-100 column indicated that additional length was needed. Separation was improved with the 700 ft

TABLE IV

Degrees of Separation[1] of Stack Gas Components

Stack Gas Component	Type of Capillary Column		
	Squalane Coating 28.7 ft	Triton X-100 Coating 425 ft	Triton X-100 Coating 700 ft
H_2S	N.S.	I.S.	I.S.
SO_2	N.S.	C.S.	C.S.
CH_3SH	(*)	C.S.	C.S.
NO_2	N.S.	N.S.	N.S.
NH_3	(*)	N.S.	N.S.
CH_4	(*)	(*)	N.S.
CO_2	N.S.	(*)	N.S.
H_2S - SO_2	(*)	(*)	React.,N.S.
SO_2 - CH_3SH	(*)	(*)	C.S.
H_2S from air[2]	(*)	(*)	N.S.
CH_3SH from air[3]	(*)	(*)	C.S.

N.S. No separation
I.S. Incomplete separation
C.S. Complete separation
(*) Not determined

[1] All single components, the separation refers to air.

[2] In the presence of mercaptans.

[3] In the presence of hydrogen sulfide.

column, although, even this length did not yield complete resolution of H_2S. Mixtures of H_2S and SO_2, plus water vapor and air, were found to react in the syringe, forming free sulfur, and therefore no peaks were obtained. Mixtures of H_2S and CH_3SH produced chromatograms with the H_2S peak displaced into the air peak, showing no H_2S - air separation, and the slight tail of the H_2S - air peak running into the mercaptan peak.

Methyl mercaptan was completely separated from air by both the 425 ft and 700 ft Triton X-100 columns, while the squalane column provided no separation. Mixtures of CH_3SH and SO_2 were almost completely separated by the 700 ft column, with the tail of the mercaptan peak just touching the SO_2 peak.

Successful separation of SO_2 was obtained by use of both Triton X-100 columns, while squalane gave no separation. The results of mixtures of SO_2 with H_2S and CH_3SH have been discussed in the previous two paragraphs. Some typical results achieved with capillary columns are shown in Figure 17.

No separation was obtained on any of the capillary columns for NO_2, CO_2, NH_3 or CH_4.

Sample sizes for all runs ranged from 0.02 to 0.05 ml for single components, and from 0.10 to 0.20 ml for mixtures. All experimental work with capillary columns was conducted at room temperature, which ranged between 20° and $29^{\circ}C$.

Additional separation data for the two Triton X-100 columns are given in Table V.

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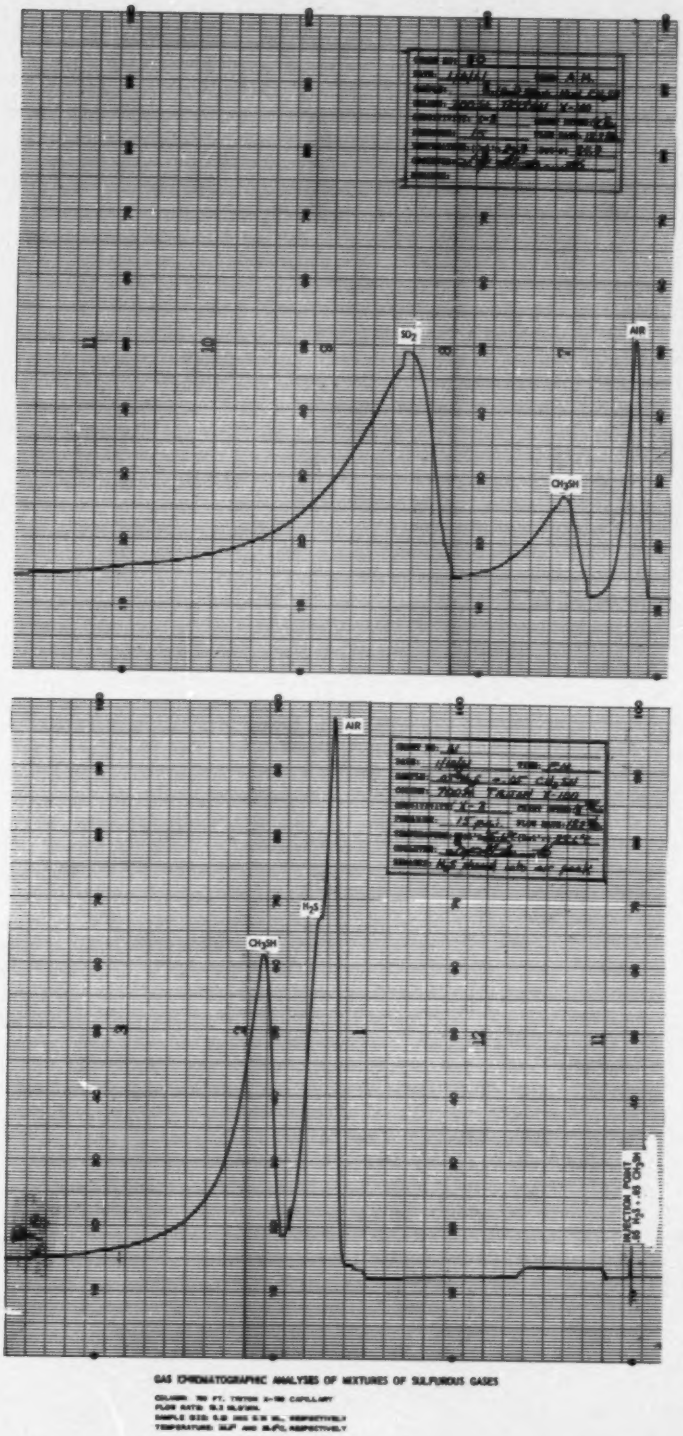

Figure 17. Typical Analyses of Mixtures on a Capillary Column

TABLE V

Retention Data Obtained from Capillary Columns

Stack Gas Component	Triton X-100 (425 ft) F. R.	R. V.	V_g^o	Triton X-100 (700 ft) F.R.	R.V.	V_g^o	R
H_2S	3.6-5.0	3.6	9.3	10.5	5.4	8.7	I.S.
CH_3SH	4.8	16.0	41.5	9.6-12.2	33.0	53.1	1.4
SO_2	(*)	(*)	(*)	11.5	85.9	138.1	2.5

F.R. = Flow rate range (ml/min)
R.V. = Retention volume (ml)
V_g^o = Specific retention volume (ml/gm coating liquid)
R = Separation factor for air and the component
I.S. = Incomplete separation
(*) = Not determined

E. Discussion of Results

Much of the experimental data between runs showed considerable variation with the exception of retention volumes, which were highly reproducible. The variation of results may be due to changes in temperature, sample size, flow rate and detector sensitivity.

Sensitivity, an index for comparison of the signal output of detectors, as defined in the Glossary of Terms, ranged from 150 to 250 for methyl mercaptan, when a filament type thermal conductivity cell was used.

The number of theoretical plates, N, for the Triton X-100 series column ranged from 235 to 546 for CH_3SH; and from 186 to 212 for SO_2. These relatively low values of N are due to the severe tailing obtained, as N is inversely proportional to the square of the peak base width (see defining equation in the Glossary).

The values for the separation factor, R, the index of separation between components as defined in the Glossary, averaged 1.4 for air - CH_3SH, 2.5 for air - SO_2, and 1.3 for CH_3SH - SO_2 mixtures on the 700 ft Triton x-100 column.

These variations of the experimental values of N and S indicate that with column coating materials and column characteristics optimized for the capillary column, controlled analyses are necessary to correlate retention volume, separation factor, and number of theoretical plates with temperature and flow rate.

The retention volumes of individual components in mixtures were found to differ with those of the pure components, as was the case with packed columns.

To check the squalane column after its failure to separate any of the stack gas components, a mixture of ether, acetone, chloroform and benzene - known to be separated by this type of column - was analyzed and satisfactory separations obtained. This experiment proved that the column was properly coated, but that it was not suitable for the separation of stack gases.

F. Experimental Difficulties

Preliminary studies with squalane and Silicone Oil 550 coated capillary columns indicated that flow rates of 5 to 10 ml/min were too high because the coating liquid was blown off the column. On the other hand, these gas flow rates were too low for the filament type thermal conductivity cell, producing an unstable base line. Therefore, a helium line to by-pass the column, as shown in Figure 18, was installed to produce a low flow rate through the column while providing a high flow rate through the thermal conductivity cell. This apparatus modification was used on the 28.7 ft squalane and 425 ft Triton X-100 columns.

During the installation of the Triton X-100 series column, a connection in the by-pass was accidentally broken and the by-pass was removed. The 700 ft series column and the detector operated successfully at flow rates of 15 to 20 ml/min for one month without the by-pass. This indicates that the Triton X-100 liquid coating has greater adherence to the nylon tubing than does either squalane or Silicone Oil and that a flow rate of 15 ml/min through the thermal conductivity cell is satisfactory. Other investigators (35) have stated that strong adherence to the capillary walls, or support material, effectively lowers the vapor pressure of the coating liquid and therefore lengthens the theoretical column life. Therefore, it is believed that other tubing materials, with a rougher inside surface, would be beneficial to increase the adherence of the coating liquid and column life.

The greatest difficulty with the chromatograms obtained from the various capillary columns was due to the strong tailing exhibited for all components. This tailing is believed to be caused by several experimental

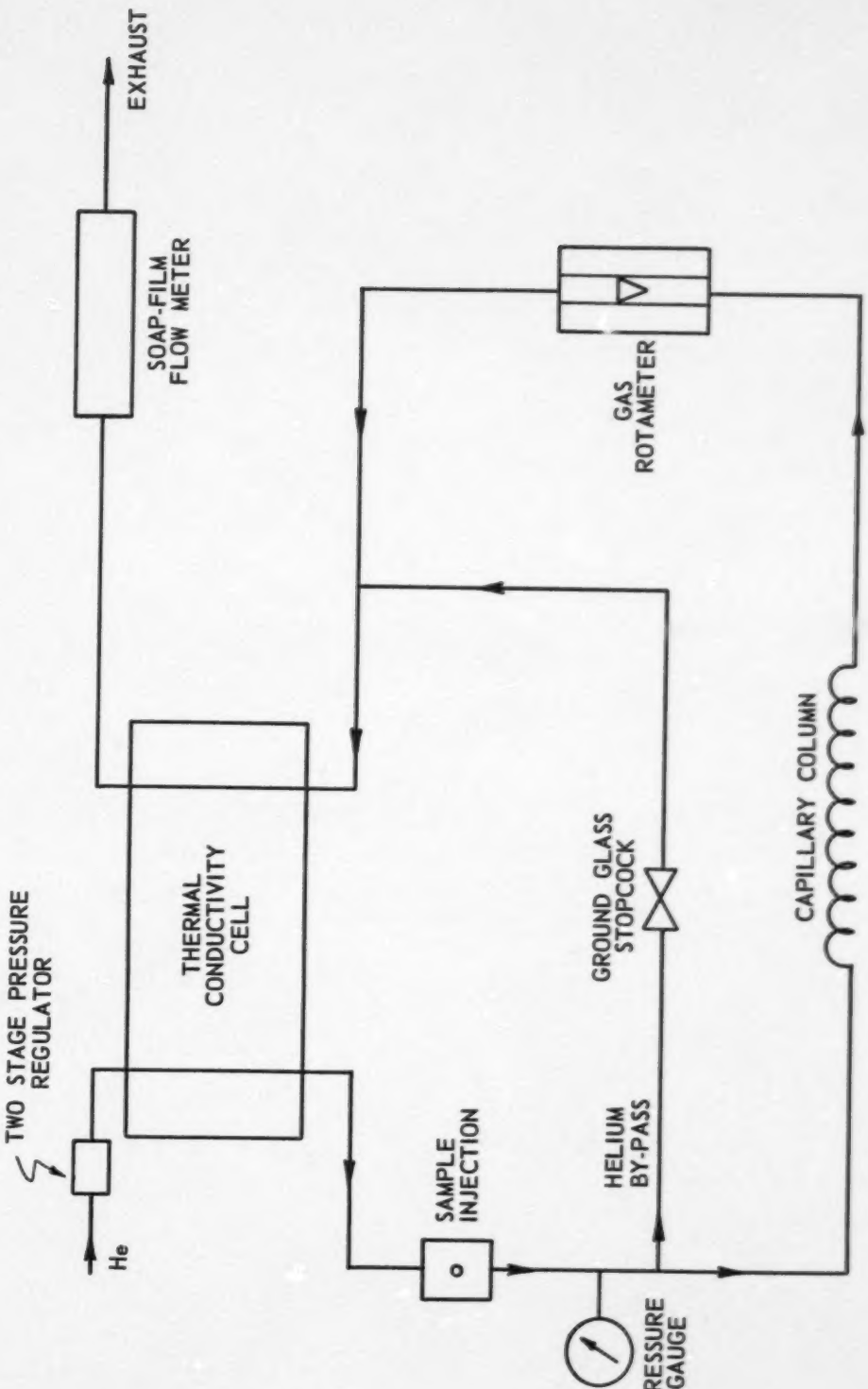

Figure 18. Flow Diagram of Capillary Columns By-Pass

steps and the apparatus, such as: syringe methods of sample injection; dead volumes in the injection and column fittings, and in the block of the filament thermal conductivity cell; as well as the unequal coating thickness of two sections, as in the Triton X-100 series column.

Due to the strong tailing of peaks, it was concluded that capillary columns would be unsatisfactory for quantitative work with the available equipment. Consequently, this phase of these investigations was not pursued further.

VII. CONCLUSIONS

It is concluded that:

1. Hydrogen sulfide, methyl mercaptan and sulfur dioxide can be quantitatively analyzed down to 100 p.p.m. on optimized Silicone Oil 550, Triton X-100, Triton X-305, and di-butyl phthalate columns.

2. Qualitative separation of NO_2, N_2O and other stack gases was readily achieved. However, the literature provides chromatographic columns suitable for the quantitative analysis of O_2, N_2, CO, CO_2, CH_4, NO_2 and N_2O.

3. The retention volumes of components in mixtures are usually affected by the presence of other gases. This difficulty is experienced by packed or capillary columns alike.

4. Capillary columns may be satisfactory for the quantitative analysis of stack gases, provided specialized equipment is available.

5. For quantitative analysis of gaseous components in the p.p.m. concentration range, the hypodermic syringe method of sample injection can not achieve highly reproducible results. Only automatic sampling valves can be used successfully.

6. Gas chromatography still holds great promise as an analytical method for stack gases and pollution analysis in general. This conclusion is enhanced by the complete success which the method is having in other fields.

VIII. SUGGESTIONS FOR FUTURE WORK IN THIS FIELD

A fair amount of research remains to be done in the analysis of stack gases. Of foremost importance is the qualitative analysis of NO, NO_2, N_2O_3 and N_2O_5. Completion of these analyses would satisfy the qualitative work on all common components.

Using available commercial equipment, all the component gases could then be analyzed in concentrations as low as 5 p.p.m., or in even lower concentrations with pre-concentration techniques, and down into the p.p.b. range for some hydrocarbons.

There remains the problem of qualitative interference between components in mixtures. It will be necessary to make an evaluation of the degree of shifting of retention times of the components in various mixtures and to correlate this information for general use.

Since it is impossible to prepare chromatographic columns reproducibly so that retention times can be duplicated, mathematical treatment of the process should be developed in order that by proper adjustment of the parameters two slightly dissimilar columns can be made to behave identically.

The final setps in the development would evolve from field testing which would result in the selection of the best methods and equipment for sample collection and injection into an analysis unit. At this point the problem of high concentrations of water vapor, usually associated with stack gases, and its effect on the analysis would be encountered and have to be dealt with.

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X. APPENDIX A - SOURCES OF ERROR IN THE GAS MIXING APPARATUS

Sources of error inherent in the gas mixing device:

(a) Gas cylinder into flask "M"
  (1) Incomplete vacuum in tubing
  (2) Air leakage
  (3) Diffusion of gases from dibutyl-phthalate
(b) Incomplete vacuum in sample flask "A"
(c) Air leakage into sample flask
(d) Non-ideality of gas
(e) Reading of manometers
  (1) Reading of scale
  (2) Scale plumb
  (3) Manometer plumb
  (4) Expansion of scale (temperature coefficient of scale material)

Table VI is a tabulation of the magnitude of these errors.

TABLE VI

Magnitude of Errors in Compound of Lowest Concentration

A. Preparation of Sample without Dilution

Item	% Error	Comments
1. Cylinder to Flask "A"	0.20%	if 1.0 cc/500 cc
2. Incomplete Vacuum	0.07%	if 0.50 mm (init. vac.)
3. Leakage	0.07%/hr	if 1/2 mm/hr rise
4. Non-ideality	0.01%	Van der Waals
5. Reading	3 @ 0.16 = 0.48%	if 1/64" error in 10" reading
6. Expansion of Scale	0.04%	
Total without Dilution	0.87%	

B. Preparation of Sample with Dilution

1. Incomplete Vacuum	0.07%
2. Leakage	0.07%
3. Non-ideality	0.01%
4. Readings	0.48%
5. Expansion	0.04%
Error per dilution	0.67%

Assuming 3 dilutions to obtain 25 ppm, the maximum total error (see Table VI) is 2.88%, or approximately 3%. Since reading errors should compensate, the average total error is less than 0.96%, or approximately 1%.

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4. Grune, W.N., Chueh, C.F. and Gutermuth, J.M., "Analysis of Oxides of Sulfur and Nitrogen by Gas Chromatography", to be presented at the Air Pollution Symposium of the National Meeting of the American Chemical Society at Atlantic City, N.J., September 9-14, 1962

XII. STAFF

The following professional personnel have been employed on this project since December 1, 1959:

W.N. Grune	Principal Investigator	Dec 1, 1959 to May 31, 1962	10% time
C.F. Chueh	Graduate Research Asst.	Dec 1, 1959 to May 31, 1962	37.5% time
R.C. Peek, Jr.	Graduate Research Asst.	Dec 1, 1959 to Jun 1, 1960	15% time
C.H. Kaplan(*)	Graduate Research Asst.	Jun 15, 1960 to Sept 15, 1961	30% time
C.H. Kaplan	Research Assistant	Sept 15, 1961 to May 31, 1962	60% time
R.V. Cribb, Jr.	Graduate Research Asst.	Jul 15, 1960 to Oct 7, 1960	65% time
Marta Glueck	Research Assistant	Oct 5, 1960 to Jan 31, 1961	90% time
J.M. Gutermuth	Technical Assistant	Oct 1, 1960 to May 31, 1962	90% time

In addition, the following students have assisted these studies on a part-time basis:

Ray Smith	Student Assistant	Jan 20, 1960 to July 1, 1960	60% time
D.F. Hill	Student Assistant	Mar 1, 1961 to May 31, 1962	40% time

(*) Mr. Kaplan was the recipient of a U.S. Public Health Service Traineeship and devoted his master's research to these studies.